DEVELOPMENT OF A HIGH PRESSURE DIGESTION TECHNIQUE AND A DATA ACQUISITION/REDUCTION PROCEDURE AND THEIR APPLICATION TO THE ICP-MS ANALYSIS OF URBAN SEDIMENTS AND SOILS FROM CEBU, PHILIPPINES

CENTRE FOR NEWFOUNDLAND STUDIES

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Development of a high pressure digestion technique and a data acquisition/reduction procedure and their application to the ICP-MS analysis of urban sediments and soils from Cebu, Philippines

by

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to Bang,
Jeng
and
Josh

Abstract

Trace element analysis in the earth and environmental sciences requires accurate and precise determination of element concentration in geological samples. Inductively coupled plasma-mass spectrometry (ICP-MS) continues to provide reliable data in this area. Analytical concerns in solution ICP-MS include completeness of digestion and volatilization loss. The work embodied in this thesis examined the use of high pressure digestion to address incompleteness of digestion in the analysis of geological materials.

High pressure digestion vessels (HPDV) fabricated in-house were compared with the existing method at Memorial University of Newfoundland which uses screw top teflon (STT) jars in digesting several geochemical reference materials (GRMs). ICP-MS analysis of the solutions using the MUN ICP-MS trace element package demonstrated more complete digestion of the marine sediment GRMs PACS-1, MESS-2 and BSK-1, indicated by higher Y, Zr, Nb, HREE, Hf and U values when the HPDV was used. Zirconium was from 40% to 150% higher, Hf was 35% to 120% higher, and the HREEs were generally higher by about 20% in the HPDV than in the routine method. The results indicate better decomposition of resistant minerals especially zircon grains that were likely in high abundance in the sediments. No significant difference between STT and HPDV was found for the other GRMs (basalt, andesite, gabbro, dolerite and syenite). Lower element values for the granite material, G-2, were obtained in the HPDV, but Zr and Hf values were still significantly higher than in the STT. Rubidium was poorly recovered in the marine sediments, the reason for which has not been determined in the study.

An ICP-MS data acquisition and reduction procedure (environmental-exploration package) was developed to determine transition metals and other trace elements in geological samples. Twenty-nine masses comprised the element suite: ^{51}V, ^{52}Cr, ^{55}Mn, ^{59}Co, ^{60}Ni, ^{65}Cu, ^{66}Zn, ^{75}As, ^{77}Se, ^{79}Br, ^{98}Mo, ^{107}Ag, ^{111}Cd, ^{118}Sn, ^{121}Sb, ^{125}Te, ^{127}I, ^{139}La, ^{140}Ce, ^{141}Pr, ^{145}Nd, ^{167}Er, ^{169}Tm, ^{175}Lu, ^{183}W, ^{201}Hg, ^{208}Pb, ^{209}Bi and ^{232}Th. Most important interferences were from $^{43}Ca^{16}O$ on ^{59}Co, $^{44}Ca^{16}O$ on ^{60}Ni, $^{49}Ti^{16}O$ on ^{65}Cu and $^{50}Ti^{16}O$ on ^{66}Zn. Internal standards used were ^{45}Sc, ^{115}In and ^{187}Re. ^{238}U and $^{254}(UO)$ were measured to monitor polyatomic ion formation. Sensitivity of the elements was calculated from one of 2 external standards, except for 3 elements which were calibrated through surrogate calibration (Sn using Sb, W using Lu, and Hg using Pb). Calibration was demonstrated to be successful for the pair Sn-Sb; though not as good for W-Lu, probably due to laboratory contamination. Surrogate calibration for the pair Hg-Pb proved unsuccessful, most probably because of volatilization loss of Hg during sample digestion. Analysis of reference materials using the new package showed excellent results for V, Co, Cr, Ni, Sn, Sb, Cu, Zn, Mo, Cd and Pb compared with literature values. Arsenic and Ag results were mostly near detection limits. Comparison with XRF results indicated good agreement between the environmental-exploration package and the XRF. Compared with the MUN ICP-MS trace element package, the new package was in good agreement for the elements Mo, La, Ce, Pr, Nd, Er, Tm, Lu, Pb, Bi and Th.

The high pressure digestion technique and the ICP-MS environmental-exploration package were applied to the analysis of urban stream sediment and soil samples from the

Philippines. Good correlation for La, Ce, Pr, Nd, Er, Tm, Lu, Pb, Bi and Th between the package and the MUN ICP-MS trace results was shown by the high correlation coefficients derived. Nickel and As gave poor results because of the high concentrations in the calibration blanks for Ni and possibly because of volatility for As. Particle size may also have influenced the results for these 2 elements because results for the reference materials indicated good agreement between the XRF and the environmental-exploration package. It was found that the GRMs are significantly finer grained than the stream sediment and soil samples (greater <53 μm fraction), suggesting that there may be a need to grind the stream sediment and soil samples to obtain better results.

Mapping of empirically derived geochemical classes showed that the spatial distribution of Cr, Ni, Cu, Zn, Pb, Sn, Sb and Cd in the stream sediments correspond to the large commercial zone in the SW portion of the study area. Higher values of Cu and Zn point to an industrial zone to the east. The soil element data correspond to an industrial zone where manufacturing and use of metal parts abound. Arsenic was high in the relatively new land development to the SW, which was a site where storm drainage and airline night soil from the nearby air facility previously collected. Except for Sb and Cd, the element concentration in the stream sediments were high for a limestone terrain. The soil samples likewise indicated input from human activity. The derived geochemical landscape coincided with the known land use in the area.

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Development of a high pressure digestion technique and a data acquisition/reduction procedure and their application to the ICP-MS analysis of urban sediments and soils from Cebu, Philippines

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Chapter 1

Scope and Purpose of the Study

1.1. Introduction

The role of inductively coupled plasma-mass spectrometry (ICP-MS) in earth and environmental sciences has continued to expand since its first commercial introduction in 1983 (Hall, 1992; Date and Gray, 1989). This role has been to cover an area where other instruments have struggled to achieve, i.e., the provision of simultaneous multi-element analysis, low elemental detection limit and a high linear dynamic range (Potts, 1987; Longerich *et al.*, 1990; Jenner *et al.*, 1990; Hall, 1992). Compared with ICP-AES (atomic emission spectroscopy), ICP-MS offers simpler spectra and the ability to obtain isotopic information (Longerich *et al.*, 1986; Date and Jarvis, 1989). Reviews of developmental work and applications to geological science problems are given in Houk and Thompson (1988); Hall (1989, 1992); Date and Gray (1989); Jarvis *et al.*, (1992); Falkner *et al.* (1995).

Many studies have concentrated on the rare earth elements (REEs) and yttrium whose accurate determination at trace to ultra-trace levels are essential in petrogenetic studies (Longerich *et al.*, 1987; Jarvis, 1988; and Doherty, 1989). The focus of the present work is on trace elements, including the first-row transition metals, the study of which is important to both environmental and exploration geochemical problems. A closed vessel

digestion method was devised to address the issue of incomplete digestion, a major source of inaccuracy in analysis (Bock, 1979) especially when samples contain resistant mineral phases. Both digestion method and analytical protocol are then applied in the analysis of stream sediment and soil samples, types of sample matrix both very useful to mineral exploration, provenance and environmental studies.

1.2. High Pressure Sample Decomposition

Although research momentum has increased for solid sample introduction like laser ablation (*e.g.*, Longerich *et al.*, 1996), current ICP-MS work is still mainly solution-based and therefore samples must be dissolved (*e.g.* Totland *et al.*, 1992, 1995; Hall, 1992). There are several methods of sample decomposition (Bock, 1979; Anderson, 1987). Among oft-cited disadvantages of dissolution methods (*e.g.*, increasing overall analysis time and the likelihood of error) are concerns that such procedures can yield low results due to volatilization loss or incomplete digestion. Incomplete dissolution can be critical to REE analysis especially since significant rare-earth elements (REEs) may reside in resistant silicate, phosphate, and oxide minerals such as zircon, monazite, and xenotime (Jenner *et al.*, 1990).

High pressure digestion has been used to address this problem in dissolving the silicates (Dolezal *et al.*, 1969; Maqueda *et al.*, 1986). Chao and Sanzolone (1992) reviewed briefly some of the available vessel types and their properties. It is part of this present study to

look into the applicability of high pressure digestion in the determination of trace elements in some geological materials, considering its potential in the accurate measurement of the REEs in these materials and therefore in their contribution to petrogenetic studies.

1.3. Analysis of Sediment Samples

Petrogenetic studies utilize chemical data mainly from whole rock samples or mineral separates to gain valuable insights about a source region's geochemical or crustal evolution (Date and Jarvis, 1989). Sediments and sedimentary rocks have similarly been used to estimate the composition of the exposed portion of the crust (Taylor and McLennan, 1985; McLennan *et al.*, 1993). Sediments can represent as wide and varied a provenance as possible or they can reflect more local variation depending on transport distance (Cullers *et al.*, 1988). In geochemical exploration, sediment analysis is popularly utilized in depicting broad geochemical landscapes or in locating anomalies in the general geochemical character of detritus (Rose *et al.*, 1979). The practice has been used, for example, in whole country programmes such as that undertaken in England and Wales (the Wolfson Geochemical Atlas, Webb *et al.*, 1978) and in Finland (Salminen and Tarvainen, 1995). More recently, analysis of clastic sediments has come hand in hand with water analysis in environmental geochemistry (Förstner and Wittman, 1979; Förstner, 1989; Heling *et al.*, 1990; Belogolova and Koval, 1995) with many studies showing that they are both a source and a sink of metals in the environment. Part of this present work will deal with the application of the digestion procedure mentioned to urban sediments and soils

from Cebu, in the Philippines, prior to analysis by ICP-MS, with the view of extracting information regarding the geochemical landscape of the area and some implications as to the levels of contaminant input.

1.4. The Transition Metals

An important focus of the present study is furthering the development of analytical methodology at the ICP-MS laboratory of the Department of Earth Sciences, Memorial University of Newfoundland. Existing ICP-MS protocols are the sinter package, the trace package, the PGE package, and the water-biological package (Longerich *et al.*, 1993a,b). The suite of elements used in this present study was proposed to complement the above packages and contribute to the analytical requirements of explorationists and environmental researchers. The analytes are V, Cr, Mn, Co, Ni, Cu, Zn, Mo, Ag, Cd, Sn, Sb, Pb, Bi, together with selected lanthanides (La, Ce, Pr, Nd, Er, Tm, Lu) and Th.

Transition metals, *e.g.*, Co, Ni, Cu and Zn, in varying combinations and usually together with Pb and Ag or some precious metals, have characterized important metallic deposits of the magmatic, Mississippi Valley or volcanogenic massive sulphide types (Govett, 1983). Nickel-Cu-Co assemblages characterize the large Voisey's Bay magmatic deposit in Labrador (Naldrett *et al.*, 1996; Ryan, 1996) whose genesis has been compared with those of other world-class Ni-Cu deposits such as Noril'sk, Sudbury and Jinchuan, including Kambalda (Naldrett, 1997).

Nickel is relatively immobile while Cu and Co are of intermediate mobility in the surficial environment. However, these three metals are easily fixed through adsorption and coprecipitation by Fe- and Mn-oxides (Rose *et al.*, 1979). The elevated Ni and Cu values of the overlying gossans at Voisey's Bay was the indication that was first noted prior to the discovery of the deposit (Naldrett *et al.*, 1996). As to environmental concerns for heavy metals, the first-row transition elements are as important as they are in exploration work. Most of them are found in the U.S. Environmental Protection Agency priority list of pollutants and are often measured in monitoring and assessment (Moore and Ramamoorthy, 1984; Adriano, 1986).

1.5. Objectives of the Study

The scope of the present work covers the main concerns highlighted in the previous sections. To summarize briefly, this work started out, firstly, to test the applicability of a high pressure dissolution procedure in addressing the difficulty in taking resistant mineral phases in geological materials into solution. Secondly, an ICP-MS data acquisition and reduction procedure was developed to determine trace elements in geological samples. Thirdly, the high pressure digestion procedure and the ICP-MS procedure were applied to samples of drainage sediments and soil. Among the suite of trace elements under study, it included the analysis of transition metals, interest in which transcends the boundary between exploration and environmental geochemistry. In effect, it affords an opportunity

to cover some of the elements not routinely determined at the ICP-MS facility of the Department of Earth Sciences, MUN (Longerich *et al.*, 1993a).

Chapter 2

Literature Review

2.1. Closed Vessel Sample Decomposition

In the evolution from the so-called classical analytical techniques through the more rapid methods of analysis, and finally into the modern instrumental methods, the integral step of dissolving a sample powder has brought challenges with respect to contamination and/or completeness of digestion. The quest for total decomposition in inorganic analysis has always contended with resistant silicate, phosphate and oxide minerals. As a consequence, increasing attention is paid to procedures which use elevated pressures (Langmyhr and Paus, 1968; Dolezal *et al.*, 1969; Warren and Carter, 1975; Bock, 1979; Maqueda *et al.*, 1986; Heinrichs, 1990; Chao and Sanzolone, 1992).

Bock (1979) traces the use of sealed containers to 1860 when Mitscherlich and Carius separately experimented with sealed glass tubes, adding that the first mention of a high pressure bomb was in a description of a design by Bertholot in 1899. Due to obvious risks of shattering, protective sheaths were utilized while utilizing a long cool down period before opening.

Indeed the choice of the vessel material is important and polytetrafluoroethylene (PTFE, teflon) has become one of the more popular materials used in high pressure digestion prior

to inorganic analysis. Besides PTFE, a range of material types has been used historically for closed vessel digestion (Bock, 1979) including glass, porcelain, fused quartz and various oxides, metals, graphite and other plastics. The following brief description of the different types is an excerpt from Bock (1979).

Borosilicate glass, for digestion vessels, was considered to be of good quality when it does not lose more than ~0.1 mg of Na_2O and a few tenths of a mg of SiO_2 while containing boiling water for a moderate time, and if it exhibits an appreciable resistance to acids (except hydrofluoric and hot phosphoric acids). Porcelain's chemical resistance is said to exceed that of glass but the material can also be vulnerable to alkalis and hydrofluoric and phosphoric acids. Porcelain can withstand high temperatures up to 1100 °C, or 1300 °C when unglazed. Of improved chemical and thermal resistance is fused quartz which can also be heated up to 1100 °C, and briefly to 1300 °C. Various ceramic oxides are used as crucibles with the advantage of being resistant to acids and alkaline melts if temperatures are not too high although they are rapidly attacked by a bisulphide melt. Their disadvantage is in their inherent brittleness and large weight due to the necessarily thick walls. Among metals, Pt is most important being acid resistant even against hydrofluoric acid and is only attacked by concentrated phosphoric acid at very high temperatures and mixtures of hydrochloric and nitric acids. Graphite is used as a crucible material in the determination of oxides in metals however a disadvantage surfaces at high temperatures when the oxides are reduced to carbon monoxide and metal carbides by the reaction with graphite.

For plastics, polythene (polyethylene, PE) is acid resistant but not against concentrated nitric acid and glacial acetic acid and several organic solvents. The main disadvantage of polythene is that it is only good up to 60 °C when it loses shape and becomes very porous to gases. Polypropylene may be used up to 110 °C and is said to be more convenient, however, polytetrafluoroethylene, or PTFE, is inert towards almost all inorganic and organic reagents with the exception of fluorine and liquid alkali melts. Porosity towards gases is considerably less than that of polythene while the working temperature range is considerably greater. Decomposition of PTFE begins at 300 °C, therefore it can be used at temperatures of up to 250 °C. The difficulty in working this material and its low thermal conductivity are cited by Bock (1979) as disadvantages. However, the results described in Chapter 3 below strongly indicate that these can be overcome.

Decomposition of geological materials especially silicates in a closed vessel is more efficient than one undertaken in an open system (Maqueda *et al.*, 1986; Potts, 1987; Chao and Sanzolone, 1992). Maqueda *et al.* (1986) described the successful dissolution of pyrophyllite using an acid mixture of 0.25 ml 65% HNO_3, 0.75 ml 37% HCl and 5 ml 40% HF in a pressure vessel lined with PTFE. Temperatures of 50, 100, 125 and 140 °C were investigated and it was shown that complete dissolution occurs optimally at 125 °C with a time of 60 min. The same material in an open system and with relatively larger acid volumes (5 ml HNO_3, 5 ml $HClO_4$ and 10 ml HF) left a white residue that was subsequently determined to be mainly SiO_2 with lesser Al_2O_3, or Fe_2O_3, and TiO_2. X-ray

powder diffraction of the residue confirmed that pyrophyllite together with rutile tends to remain undissolved using atmospheric pressure acid digestion even after several treatments.

The use of PTFE in pressure digestion of silicate materials is also described in Langmyhr and Paus (1968, 1969, 1970), Hartstein *et al.* (1973), and Warren and Carter (1975). Langmyhr and Paus (1968) utilized a temperature range from 150-250 °C in dissolving powders of reference materials G-2 (granite) and W-2 (diabase) to determine Si, Al, Fe, Mg, Ca, Na, K, Ti and Mn. The usual acid mixture of HNO_3, HF and HCl was employed, and complete digestion was reported even with digestion time as short as 10 min. In a later work Langmyhr and Paus (1970) added Cu, Pb and Zn to their analytical suite and success was similarly reported especially for the determination of trace elements in ferrosilicon. They note that the addition of boric acid brings precipitates into solution. Hartstein *et al.* (1973) utilized 3 ml HF and 6 ml HNO_3 in Teflon bombs in analyzing coal samples for the elements Be, Cd, Ca, Co, Cu, Li, Mg, Mn, Ni and K. To complex free F^- ions, boric acid (2.8 g) was added to the solution before analysis. Warren and Carter (1975) described successful matching of published values for the elements Cu, V, Cr, Ni, Co and Ba in the geochemical reference materials AGV-1 (andesite), BCR-1 (basalt) and GSP-1 (granodiorite). Complete digestion was reportedly achieved with 6 ml concentrated HNO_3, 5 ml 60% $HClO_4$ and 20 ml 60% HF in Teflon bombs at 100 °C for one hour.

Totland *et al.* (1992) utilized a commercially available microwave digestion system, the CEM® MDS-81D (CEM, Indian Trail, North Carolina, U.S.A.), in determining a suite of major and trace elements in a wide range of standard reference materials. The system was designed in an effort to improve efficiency,and time of high pressure digestion,compared with PTFE-lined vessels in conventional ovens. It introduces improved PTFE vessels that use microwave energy to speed up heating and acid reaction. The reference materials' composition spanned from ultrabasic through undersaturated intermediate to acidic igneous rock (e.g., UB-N, BHVO-1, AGV-1, STM-1, G-2) and sedimentary rocks from clastic to chemical (e.g., SCo-1, MAG-1, CCH-1, DWA-1). The use of the microwave system enabled digestion times of around 20 min, repeated for like periods when undissolved portions remained. Most elements studied produced excellent results except for Zr and Hf which invariably gave low values compared with published values.

While the above authors describe the relative facility in dissolving substances within shorter time periods, the literature also has specific studies that dealt with the analysis of particularly resistant phases in analyzed materials that entailed longer decomposition times (Dolezal *et al.*, 1969).

Dolezal et al (1969) designed a digestion assembly with a PTFE crucible of 25-30 ml capacity. The apparatus was used to decompose minerals known for resistance to normal modes of acid attack. Among these minerals and substances were corundum, silica (glass sand), tin dioxide (cassiterite), synthetic anatase, synthetic rutile and zircon. They cite that

in the case of tin dioxide, none of the usual methods of decomposition for the natural variety (sulpho-alkaline decomposition, fusion with sodium carbonate mixed with borax or sodium peroxide, etc.) are suitable for determining the presence of Pb, Bi, Sb, Cu and other impurities due to the formation of corrosion products with the vessels normally used. The use of their design enabled complete dissolution of 2 g tin dioxide within 6 h (with 15 ml 38% HCl or 48% HBr). After volatilization of tin(IV) bromide, all the trace components were reportedly determined with a high precision. Results for most of the other substances were shown to reach 100% decomposition using varying combinations of acids and different decomposition times. These include andalusite, beryl, cerium dioxide, anatase, rutile, magnetite, staurolite and tourmaline, with decomposition times ranging from 3 h (for CeO_2) to 16 h (for rutile). Near-complete dissolution (>99%) was shown for pyrite, spinel, chromite, microcline and lepidolite. Zircon achieved a decomposition of <50%. It was digested only with 25 ml 38% HF; no other acid type or combination was apparently attempted for this mineral.

For many materials, the effect of decomposition time was evident, *e.g.*, for rutile which showed complete dissolution in 22 ml of H_2SO_4 after 16 h and attained 99.6% decomposition after 5 h. Aside from dissolution times, an important note was also made on the particle size for these substances. While the results described above were obtained from experiments done on the minus 200 mesh size fraction, a portion of the study by Dolezal *et al.* (1969) investigated the effect of changing particle sizes. The material selected was corundum and this showed that excessively ground corundum becomes more

difficult to decompose than the same material ground to conventional particle size for analysis.

2.2. Sedimentary Geochemistry

The chemical information derived from sediments has been used as a basis to estimate the composition of the crust that is exposed to weathering (Taylor and McLennan, 1985). Interpretations of provenance and tectonic setting of ancient terranes are numerous in the literature (*e.g.*, Bavinton and Taylor, 1980; Bhatia, 1985; McLennan *et al.*, 1993). A provenance study of a more recent setting by Norman and de Deckker (1990) describes the elemental contribution by weathering of Mesozoic and Proterozoic sedimentary rocks during marine transgression over a Late Quaternary lacustrine environment of the Gulf of Carpentaria in northern Australia.

The mechanism of weathering, together with glacial erosion, is a natural sampling process that mixes and homogenizes upper crustal material. It involves two major processes that disperse elements from the source into receiving sedimentary basins. These are dissolution in natural waters of relatively soluble elements and the mechanical transport of the relatively insoluble constituents like Zr and the rare-earth elements. Taylor and McLennan (1985) note that elements such as Zr are strongly dispersed during clastic transport and therefore have limited value in estimating crustal composition. On the other hand, the REEs, together with Th and Sc, which are less fractionated by sedimentary processes, are

very useful for such purposes. Nevertheless, Zr is well accepted as an integral component in discrimination diagrams, *e.g.*, for basalt and andesites (Rollinson, 1993; Pearce and Cann, 1973) and therefore provenance work may be applicable for sedimentary zircons from first-order streams over a terrain with a single parent rock material. Additionally, interest in zircons remain significant because of the mineral's use in U-Pb geochronology (Parrish, 1987; Roddick *et al.*, 1987), and its importance in accurate determination of Hf and the HREEs which are usually associated with Zr in rocks of continental affinity (Taylor and McLennan, 1985).

The use of trace element composition of locally derived weathering products to determine provenance has been studied by Cullers and co-workers in soils and stream sediments produced from silicic plutonic rocks in Montana and Georgia, U.S.A. (Cullers, 1988; Cullers *et al.*, 1988). In the study in Georgia, the silt sized fraction of the sediments derived from intense weathering of a granitic terrain gave values for Rb, REE, Th, Ta, Fe, Co and Sc and the ratios La/Sc, Th/Sc, La/Co, Th/Co, Eu/Sm and La/Lu closest to the respective concentration in the source rocks (Cullers, 1988). The REE patterns of the clay sized fraction are similar to those of the source substantiating Taylor and McLennan's (1985) conclusion that the bulk of REEs preserved in sedimentary rocks resides in this size range. Patterns in the silt and clay portions are actually similar although the silt tends to have lower total REE.

The concentration of the REEs was measured in different size fractions in sediments and soils found over a variety of parent rocks in Montana (Cullers *et al.*, 1988). Although there was correspondence between sediment and source using element ratios La/Sc, Th/Sc, La/Co, Ba/Sc and Ba/Co, the REE patterns of the source rocks were not necessarily preserved in the sands. Cullers *et al.* (1988) inferred that these characterizing trace elements may have weathered out into the clay mineral fractions.

The general inverse relationship between metal content and particle size has also been taken advantage of in exploration geochemistry (Rose *et al.*, 1979; Fletcher, 1981). It is accepted that most of the anomalous metal in stream sediments is usually associated with the finer size fractions. However, there seems to be lesser restriction for explorationists considering that the minus 80 mesh fraction (< 177 μm) has usually given an acceptable contrast in detecting anomalous metal concentrations from background levels in soils and sediments. In examples of total and exchangeable heavy metal (Cu, Pb, Zn) content in stream sediments from New Brunswick, Uganda and Zambia, Rose *et al.* (1979) illustrated the applicability of this size fraction in maximizing the variation and contrast between sediments from mineralized and non-mineralized areas even though this range did not give the greatest absolute values.

Much of exploration geochemical work has also looked at over-all geochemical landscapes in establishing geochemical provinces. Broad-scaled variations need to be well defined before target anomalies can be recognized. Sources of the larger-scaled or

regional variations are characterized; usually these are lithological in nature but they can also be in response to factors like the presence or lack of vegetation, degree of soil cover and/or weathering, terrain elevation, etc. Total metal content has been used to describe geochemical landscapes as exemplified in Finland (Salminen and Tarvainen, 1995) and in the pioneering Geochemical Atlas of England and Wales (Webb *et al.*, 1978). The work begun in Finland reflects the world-wide transformation from a purely exploration focus to one that considers environmental implications of geochemical data obtained from surficial environments. Sampling of different media under different scales or sampling density has given an overview of the geochemical terrain and allowed a consolidation of geochemical information that are subsequently made available for evaluation of exploration or environmental importance (Salminen and Tarvainen, 1995).

Analysis of clastic sediments for environmental purposes operates on the premise that they are both a sink and a source of contaminants (Förstner *et al.*, 1990). Although determination of anthropogenic input commonly involves the exchangeable metal portions in the sediments, the total metal content is also measured as part of characterizing the substrate with the purpose of evaluating potential releases induced by pH changes. General identification and evaluation of sources and their distribution benefit from the measurement of the total metal content as well as the determination of the sediment's mineralogy including its major lithic component. Significant presence of lithic carbonate fragments, for example, plays a role in the acid-consuming ability of a particular sediment,

specifically in providing buffering capacity against [H^+] ions that may come from the oxidaton of metal-bearing compounds (Förstner *et al.*, 1990).

2.3. Transition Elements

For this study, selection of elements to be measured by ICP-MS was spurred by interest in inorganic indicators applicable in the assessment of an urban surficial environment. An important consideration was the prevalence of heavy metal sources in the study area, the lack of basic geochemical information and the presence of 5 streams passing through the urban center. The first-row transition metals (V, Cr, Mn, Co, Ni, Cu, Zn) were appropriate as analytes of choice and have been part of many environmental monitoring programs together with the elements As, Cd, Pb, Hg and others (Moore and Ramamoorthy, 1984; Adriano, 1986; Hart and Hines, 1995). Most of these are outlined in the U.S. EPA's priority list of pollutants.

The transition (*d*-block, IUPAC groups 3-12) elements have properties transitional between the highly reactive metallic elements of the *s*-block (IUPAC group 1-2), which typically form ionic compounds, and those of the *p*-block (IUPAC groups 13-18), which are largely covalent (Lee, 1996). The 10 first-row transition elements are considered reasonably common in the earth's crust and are estimated to make up 6.79% of its mass. Three of these are very abundant, with Fe as the fourth most abundant element by weight;

Ti as the ninth; and Mn the twelfth. Their important collective use in industry has attracted significant mineral exploration for their deposits since the beginning of civilization.

In modern times, the first-row transition metals are showcased in world-renowned ore-bodies. In varying combinations with each other or with other elements like Pb, Ag, or the platinum group elements (PGEs), they have distinguished several magmatic, Mississippi Valley type, or volcanogenic massive sulphide deposits (Govett, 1983). Nickel-Cu-Co characterizes the large Voisey's Bay magmatic deposit in Labrador (Ryan *et al.*, 1995; Naldrett *et al.*, 1996; Ryan, 1996; Lightfoot, 1998), counting it as one of the major recent discoveries of its type, and affording a new venue for the study of metallogenic, structural and geochemical relationships in addition to other world-class Ni-Cu deposits in Noril'sk (Russia), Sudbury (Canada), Jinchuan (China) and Kambalda (Australia) (Naldrett, 1997).

The literature cited above underscore the importance of chemical measurements in the study of the transition metals. Analytical concerns relative to these elements in geological materials, however, are seldom reported in the literature. Of what is available, two papers stand out and these are from the Chemistry Division of the National Research Council of Canada in Ottawa (McLaren *et al.*, 1987, 1988). Both have described the analysis of sediment reference standards (BCSS-1 and PACS-1, respectively) and some of the procedural interventions necessary in the accurate determination of the transition elements in similar matrices using ICP-MS. These sediment reference materials were analyzed for their contents of some transition metals (V, Mn, Co, Ni, Cu, Zn, Cd, Mo) and also As and

Pb. For PACS-1, Cr, Sr, Sn, Sb, Hg and Tl were additionally measured. Among other analytical considerations, the effect of the major elements, particularly the interference of Ca and Ti, on Co, Ni, Cu and Zn, was studied and quantified. The oxides and hydroxides formed by these 2 major elements were noted to cause an enhancement of the signals of the transition metals. Standard addition and external calibration were the methods used in the determination by ICP-MS of the transition metals in BCSS-1 (McLaren *et al.*, 1987); while internal standardization was employed in the analysis of PACS-1 (McLaren *et al.*, 1988). They noted that the argon dimer $^{40}Ar_2$ seemed to work better for ^{75}As and ^{86}Sr than for the first row transition elements and Mo because of closeness in mass of As and Sr to the argon dimer (*m/z* 80).

In the present study, these transition metals and other trace elements were also the main target analytes. The development of the ICP-MS analytical package to measure these elements involved the use of multiple internal standards to encompass the range of analytical masses studied, as well as the use of several calibration strategies (external calibration, surrogate calibration) and correction methods.

Chapter 3

Applicability of a High Pressure Digestion Technique to the Analysis of Geological Materials

3.1. Introduction

Decomposition of geological materials in a closed system has a decided advantage over one in an open system as reaction times are faster, and higher temperature and pressure are applied to more quickly dissolve the sample (Langmyhr and Paus, 1968; Dolezal *et al.*, 1969; Warren and Carter, 1975; Bock, 1979; Maqueda *et al.*, 1986; Anderson, 1987; Chao and Sanzolone, 1992). Polytetrafluoroethylene (PTFE) or Teflon® has become the material of choice in the construction of closed vessels because of its inert property toward most reagents. Designs have been described in many publications, *e.g.*, Langmyhr and Paus (1968), Bock (1979) and others. For the present study, fabrication of vessels followed a design detailed by Heinrichs (1990).

3.2. Material and Fabrication of Vessel

The raw material required for manufacturing the closed vessels was "virgin" PTFE (stock # 600-225, Warehoused Plastic Sales, Toronto, Ontario, Canada), which was purchased as rods with a 55 mm diameter. Before any machining work was done on the rods, they were placed overnight in an oven at 200-220°C to expose them to the temperature in which the

final vessels would be used, and to expel whatever gas the material might have in its structure. Upon cooling, the following day, the teflon rods were machined into individual reaction vessels.

Each PTFE vessel measures 55 mm in height with a volume of about 25 ml. Each cap fits snugly on top of the vessel. Before final polishing of the PTFE surfaces, the set was assembled and placed in the oven overnight at 200-220 °C. By the following morning, after cooling, fine polishing of the surfaces especially of the vessel and cap that come in contact with each other was completed. After polishing, the PTFE vessels and caps were cleaned by immersing them in a large beaker with aqua regia (3 : 1, HNO_3 : HCl) and heated to about 70 °C for about an hour. After allowing the acid to cool, the vessels were removed and washed in nanopure water, then transferred to a large beaker with 8 N HNO_3, and placed on a hot plate at 70 °C overnight. The following day, the vessels and caps were washed with nanopure water and allowed to dry near a fume hood supplied with a source of HEPA-filtered air. These were then ready for use. Prior to its first use, the assembly was put together with only acid (2 ml 8 N HNO_3 and 1 ml HF) as the vessels' content and placed in the oven at 200 °C overnight to check for reagent loss when heating. This trial showed no detectable reagent loss.

Although extra precaution is exercised to maintain the sample preparation room as clean as possible (e.g., use of clean bench techniques, etc.), there may be not-so-obvious sources of contamination that could degrade the environmental quality in the room. The supply of

HEPA-filtered air that directly dries off the washed vessels reduces the risk from air particulates as a source of trace metal contamination.

The first assembly consisted of 6 containers or "bombs" (Fig. 3.1) arranged in a circle and held in position individually by a threaded steel bolt the tip of which fits into the hole at the center of a stainless steel "coin" situated on top of the PTFE cap. During actual use, the bolts are tightened only with the use of the fingers as too much tightening might result in container deformation during the digestion phase when the teflon material expands at high temperatures. Protection from expansion is also ensured by a stainless steel ring holding each vessel. This ring also helps to distribute heat uniformly around the bomb, and keeping it in position.

Two additional sets of 6 vessels each were fabricated after results of the experiment described below were found to be satisfactory. In all, 3 sets (18 vessels total) can be used simultaneously. Oven temperature used ranged from 180 to 200 °C. Cleaning of used vessels was done by overnight immersion in 8 N HNO_3 on a hot plate at 70 °C.

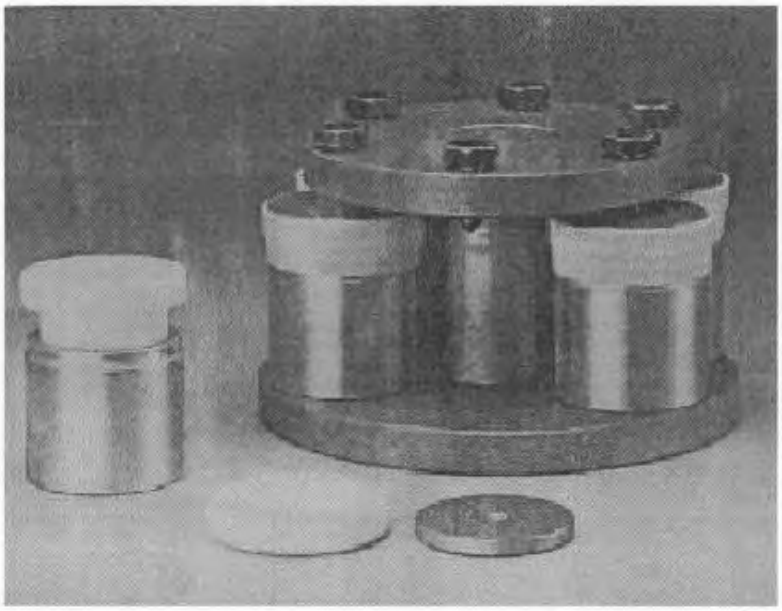

Figure 3.1. Assembly of 6 high pressure digestion vessels. (from Heinrichs, 1990)

3.3. Experimental

To study the effect of using a high pressure digestion technique and its applicability in the analysis of geological materials at the ICP-MS unit of the Department of Earth Sciences, MUN, 12 geochemical reference materials were selected for digestion utilizing the existing method for HF-HNO_3 acid digest at MUN (Longerich *et al.*, 1993a) and the high pressure method under study. Rock powder weights, unit volumes of acids added and dilution to final weights were maintained for these 2 methods. The reference materials ranged from marine sediment to andesite, basalt, diabase, gabbro, granite and syenite (Table 3.1). Unfortunately, no soil standards were available. Materials were selected to reflect a wide variety of sample matrices as well as those expected of typical environmental and exploration studies.

3.3.1. Reagents

Acids used in the study were of certified American Chemical Society (ACS) grade. Concentrated nitric acid was from Fisher (16 M, B.D.H. ACS 579-43). Hydrofluoric acid was also from Fisher (ACS 49% v/v). All reagents used in the ICP-MS unit of the Department are routinely doubly distilled to minimize the blank used in the analyses.

Table 3.1. Geochemical reference materials used to test the high pressure digestion technique.

GRM	Source	Description
BSK-1	USGS	Bottom sediment, Kesterson, California,
MESS-2	NRCC	Marine sediment, Beaufort Sea
PACS-1	NRCC	Marine sediment, harbour of Esquimalt, British Columbia
AGV-1	USGS	Andesite, east wall of Guano Valley, Lake County, Oregon
JB-1a	GSJ	Basalt, Kitamatsuura, Toge, Sasebo, Nagasaki Prefecture; replacing JB-1
BCR-2	USGS	Basalt, Columbia River, Oregon; replacing BCR-1
NBS-688	NIST	Basalt
DNC-1	USGS	Dolerite, North Carolina;
MRG-1	CCRMP	Gabbro, Mount Royal, Montreal, Quebec
G-2	USGS	Westerly Granite, Sullivan quarry, Bradford, Rhode Island
SY-2	CCRMP	Syenite, Bancroft area of eastern Ontario
SY-3	CCRMP	Syenite, same location as SY-2; blended with concentrate rich in albanite, betafite, uraninite to get product high in uranium, thorium, rare-earth elements.

USGS = United States Geological Survey;
NRCC = National Research Council Canada;
GSJ = Geological Survey of Japan;
NIST = National Institute of Standards and Technology;
CCRMP = Canadian Certified Reference Materials Project

Preparation of acids was done in two-bottle Teflon® stills and diluted with distilled, deionized (Barnstead Nanopure II) water which is rated at a minimum resistivity of 17 $M\Omega \cdot cm^{-1}$. Oxalic acid (B.D.H. ACS) and boric acid (Anachemia ACS) were in a powdered crystalline form and made up to the required volume. Two standards, designated as A and B, were prepared from stock solutions and powders from SPEX Industries Inc. (Metuchen, NJ). Rare earth elements were pure metal standards from Ames Laboratory (Ames, Iowa). All containers, bottles, tubes and micropipette tips used were rinsed with 2 M nitric acid, then rinsed with water and dried at a fume hood supplied with HEPA-filtered air, before use.

3.3.2. Existing HF-HNO_3 Acid Digest

The existing HF-HNO_3 sample dissolution for ICP-MS analysis of silicate materials at the Department of Earth Sciences, MUN, is described in Longerich *et al.* (1993). The geochemical reference materials listed above were digested using this technique which utilizes a screw-top teflon vessel, referred to below as STT. To outline briefly, approximately 0.1 g of sample powder was weighed into a clean, dry screw capped teflon vessel (15 ml capacity, Savillex®, Minnesota, USA). About 2 ml 8 N HNO_3 and 1 ml 30% HF were added while swirling the container. The cap was put on (finger tight) and the vessel placed on a hot plate at 70 °C for 2 days. The cover was then rinsed with 8 N HNO_3 and the solution was evaporated to dryness. After cooling, 2 ml of 8 N HNO_3 and 1 ml of HF were added again. The cover was replaced and the sample was set on a hot plate

at 70 °C for 2 or 3 days. The cover was then removed and rinsed with 8 N HNO_3 and the sample was allowed to evaporate. Two ml of 8 N HNO_3 and 1 ml of 2.8% boric acid were then added and subsequently evaporated. Two ml of 8 N HNO_3 were added again and evaporated. This addition of 2 ml 8 N HNO_3 was repeated and evaporated each time. Finally, 2 ml 8 N HNO_3 were added, the cover replaced and the vessel warmed gently to dissolve the residue. The solution was then transferred to a clean (acid-washed), dry polypropylene container (Corning® 120 ml). The teflon vessel and cap were rinsed with nanopure water with the rinse added to the solution. Then, 0.665 ml HF/boric acid solution (0.453 M boric acid, 0.108 N HF) and 1.35 ml oxalic acid (0.222 M) were added into solution, which was then made up to a final weight of approximately 60 g with nanopure water.

As a step to ensure more complete digestion of accessory minerals such as zircon, the second digestion phase was sometimes extended for more than 3 days. When undissolved residues remain, addition of 2 ml 6 M HCl was made and this was evaporated to dryness. After which this was taken to dryness twice with 8 N HNO_3 to minimize chloride species. If still-undissolved residues remain, these were removed by filtering.

3.3.3. Digestion Procedure Using High Pressure Vessel

The same sample powder weight was used for the digestion procedure using the fabricated high pressure teflon vessel. Approximately 0.1 g sample powder was weighed into a clean,

dry high pressure (HP) vessel. Into the vessel was added 3 ml 8 N HNO_3 and 2 ml 30% HF, swirling it until the acids covered the sample powder. The teflon lid was put in place and the vessel was set into the assembly. Up to 6 HP vessels were assembled. Bolts were tightened (finger tight) and the assembly was placed in the oven (200 °C) for 12 to 16 h or overnight. When the assembly was sufficiently cooled (usually from 1 to 2 hr at room temperature), each container was carefully opened. Special precaution was exercised in rinsing the lids with a few ml of 8 N HNO_3 because of the lid being constructed in a way that liquid could easily roll of the edge when the lid is held upside down. The opened vessel, with the stainless steel ring still holding it, was then set on a hotplate at 70 °C and the sample was evaporated to dryness. Two ml of 8 N HNO_3 and 1 ml of 2.8% boric acid were then added and evaporated to dryness. The boric acid was added to complex F^- ions resulting from the addition of HF. Then 2 ml of 8 N HNO_3 was added again and evaporated to dryness. This addition of nitric acid was repeated and likewise evaporated. Finally, 2 ml 8 N HNO_3 were added, the cap replaced and the vessel warmed gently to dissolve the residue. The solutions were then transferred to clean, dry 120 ml polypropylene containers, rinsing the HP vessel and cap with nanopure water, the rinse being added to the solution. Then, 0.665 ml HF/boric acid solution (0.453 M boric acid, 0.108 N HF) and 1.35 ml oxalic acid (0.222 mol/l) were added. The final weight of approximately 60 g was made up with nanopure water. Digestions using the high pressure vessel can be completed in 2 days compared with 6 to 8 days for the usual method employing the screw top teflon.

3.3.4. Inductively Coupled Plasma-Mass Spectrometric Analysis

The sample solutions from the two digestion methods were analyzed using the ICP-MS "trace package" at the Department of Earth Sciences, MUN (Jenner *et al.*, 1990; Longerich *et al.*, 1993). Masses measured were ^{7}Li, ^{85}Rb, ^{86}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{95}Mo, ^{133}Cs, ^{137}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{145}Nd, ^{147}Sm, ^{151}Eu, ^{157}Gd, ^{159}Tb, ^{160}Gd, ^{163}Dy, ^{165}Ho, ^{167}Er, ^{169}Tm, ^{173}Yb, ^{175}Lu, ^{177}Hf, ^{181}Ta, ^{203}Tl, ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{209}Bi, ^{232}Th, ^{238}U and ^{254}(UO). A run of samples for this package consists of 27 samples, including reference materials, reagent blanks, and duplicates. A run consists of 9 cycles in which each cycle is comprised of 12 solutions: 2 standards, 1 flush, 1 calibration blank (0.2 N HNO_3), first sample, first sample (spiked), flush, second sample, second sample (spiked), flush, third sample, third sample (spiked). The spike to the second set of samples was added off-line at 1:1 with a solution containing Li, Sr, Zr, Cs, Ba, La, Pr, Nd, Sm, Er, Tm, Bi and U. Calibration for most elements is from the 2 external standards, except for Nb, Mo and Ta which are calibrated using Zr or Hf as surrogates. The 2 external standards are: Standard A (Li, Rb, Sr, Y, Zr, Cs, Ba, La, Ce, Pr, Tb, Dy, Ho, Er, Tm,Yb, Tl, Pb, Bi, Th and U; Standard B (Rb, Cs, Ce, Nd, Sm, Eu, Gd, Lu and U).

The instrument used was a SCIEX (now Perkin Elmer) ELAN® model 250 ICP-MS (Thornhill, Ontario, Canada). Changes to the original instrument have been implemented since its acquisition, and these modifications have been described in Longerich *et al.* (1986), Longerich (1989a, b, c) and Jackson *et al.* (1990). The use of an automated

peristaltic pump controller to improve the wash and sample solution uptake rates was devised and implemented (Longerich, 1993).

Data were acquired using software supplied by SCIEX. Total counting time per mass was 10 s; dwell time per mass was 0.05 s. Dwell time is the length of time spent acquiring intensity data at one mass before jumping to the next mass. Data reduction was done off-line using a commercial spreadsheet software program (Lotus). In the data reduction, all samples and standards were background corrected using the mean of all calibration blanks in that particular ICP-MS run. Interference of the oxides, *e.g.* of ^{135}Ba on ^{151}Eu, of ^{144}Nd and ^{144}Sm on ^{160}Gd, and of isobaric overlaps (^{160}Dy on ^{160}Gd), were calculated and corrected using corresponding factors normalized to the UO/U in the sample relative to the UO/U in the standards.

Indium was used as internal standard (Longerich, 1997, pers. comm.). The In solution was pumped into a "Y" connector resulting in a combined solution that is 1 part spike (In) and parts sample. Drift correction was applied using the intensity of In.

3.4. Results and Discussion

3.4.1. High Pressure Digestion Vessel and Screw Top Teflon

Comparison of the two digestion methods (using the high pressure digestion vessel, HPDV, or the screw top teflon, STT) was made by examining the results from analysis of both digests using the Memorial ICP-MS trace package for the standard reference materials in the study. The selection of elements in this existing package covers most of those that are essential in the study of upper mantle-crustal processes and petrogenesis where the need for accuracy and precision is required especially for such elements that are critical for evaluation of geochemical models. The results utilizing this MUN trace package have been shown to compare very well with published values as applied in the analysis of U.S.G.S. standards AGV-1, BCR-1, BHVO-1 and W-1 (Jenner *et al.*, 1990). In the present study, we hoped to show the effectiveness of the high pressure vessel with emphasis on those elements that had proved difficult to recover because of incompleteness of digestion of minerals that contain them (Dolezal *et al.*, 1969; Totland *et al.*, 1992). These elements include the high field strength elements Zr, Hf and the heavy REEs (HREEs) that are commonly associated with accessory minerals such as zircons, xenotime, apatite, spinels, or oxides. Dolezal *et al.* (1969) reported a mere 50% recovery of Zr values from zircons with the use of their high pressure method. Poor recovery of Zr and Hf values from reference materials was also reported by Totland *et al.* (1992) even with microwave digestion as the technique used. The MUN analytical protocols employ an

alternative technique (Na_2O_2 sinter procedure) for samples that have been determined to contain such mineral phases (*e.g.*, by prior x-ray fluorescence spectrometry, XRF) (Longerich *et al.*, 1990; Jenner *et al.*, 1990). Although XRF analysis serves as an important quality control tool in this laboratory and works well in tandem with the MUN ICP-MS trace package for trace element determination, it would be worthwhile to develop a digestion technique that has the potential of being routinely utilized for materials known or suspected to contain hard-to-decompose mineral phases.

Four and three replicates, respectively, of the sediment geochemical reference materials, PACS-1 and MESS-2, were digested using the high pressure vessels. Two replicates were used for BSK-1, AGV-1, NBS-688 and JB-1a, while only one was analyzed for BCR-2, DNC-1, MRG-1, G-2, SY-2 and SY-3. It would have been ideal to have results from more replicate analyses before any comparison is made for all the reference materials, however, the sediment GRMs, PACS-1 and MESS-2, were emphasized because of their projected use in the subsequent analysis of sediment samples from the Philippines. For this study, comparison for the other reference materials was nevertheless undertaken as these comprise other matrix types that are potentially useful in exploration and environmental studies.

The results for the 12 geochemical reference materials are summarized in Appendix A as the mean and standard deviation of several replicates. In Fig. 3.2 are X-Y plots for these 12 reference materials and the results indicate reasonable agreement between those from

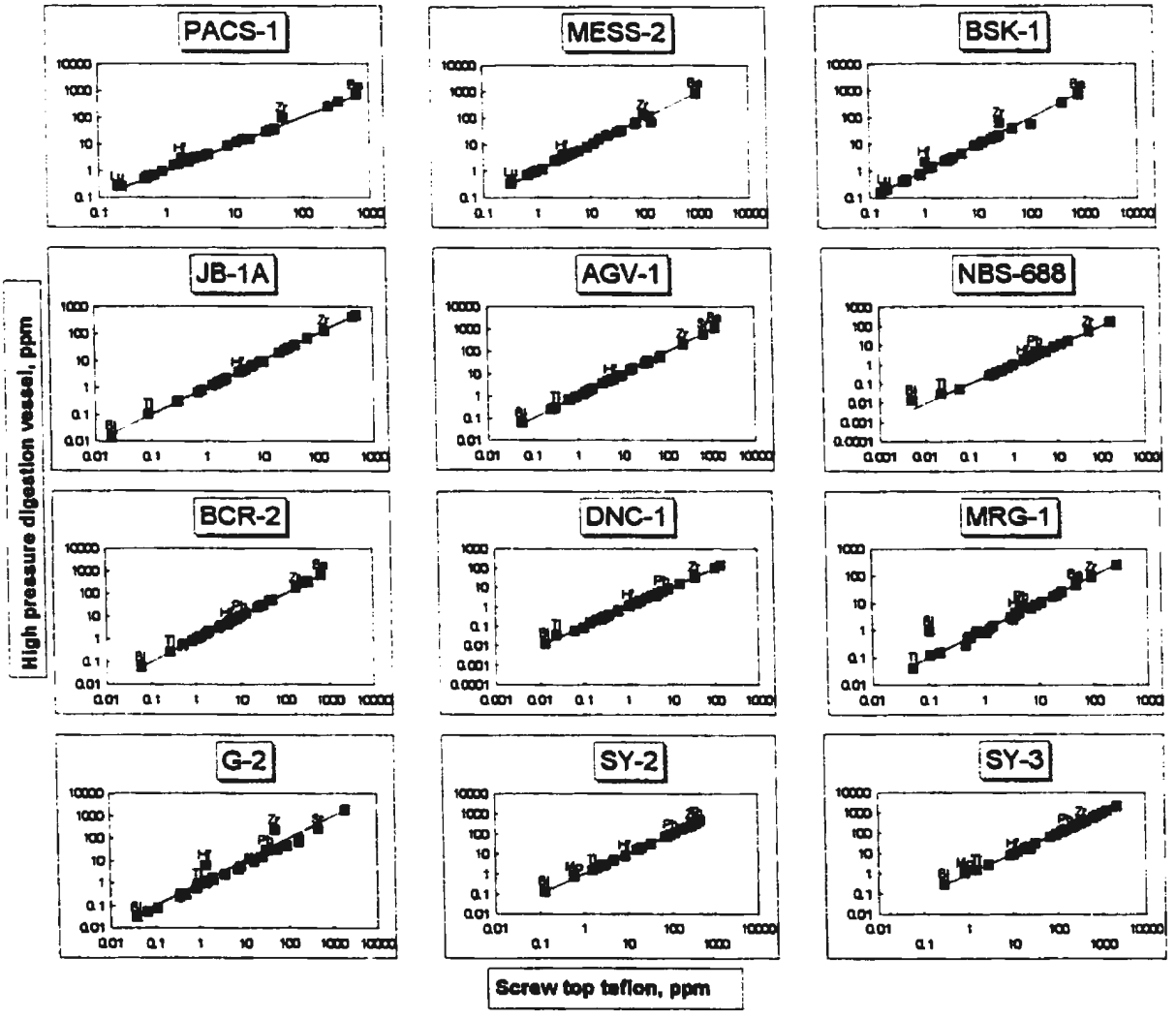

Fig. 3.2. XY plots for 12 geochemical reference materials comparing ICP-MS results from 2 digestion methods: high pressure digestion vessel (HPDV) and screw top teflon (STT).

the high pressure digestion vessel (HPDV) procedure and those from the screw top teflon (STT) method which is the digestion technique routinely used for the MUN ICP-MS trace element package. There are, however, a few elements that stray away from the 1:1 line, including Zr and Hf, notably in the sediment GRMs. There are no reported Zr and Hf values for these marine sediment GRMs (PACS-1 and MESS-2) (McLaren *et al.*, 1988; NRC, 1995) thus the difference in the results between HPDV and STT for these 2 elements can not be evaluated in terms of closeness to "true values". However, it is clear that the HPDV was giving higher values for Zr and Hf, indicating better decomposition of resistant minerals in the sediments.

A *t*-test was performed on the data to establish whether the means are significantly different between methods. A compilation of computed *t* values is shown in Table 3.2 for 5 of the geochemical reference materials that had at least two replicates analyzed per method. The table values of *t* are shown, which correspond to the pooled degrees of freedom (d.f. = 4 for PACS-1 and MESS-2; d.f. = 2 for BSK-1, AGV-1 and JB-1a) and a level of significance, α, of 10% (5% at each tail). The agreement between methods was shown for most of the elements by the *t*-test, especially for JB-1a and BSK-1, which had 26 and 24, respectively, of the 30 elements indicating that there was no evidence to suggest that the HPDV and STT means were different. PACS-1 and MESS-2 each had 13 elements indicating no significant difference, while AGV-1 had 18 elements.

Table 3.2. Computed *t* values to establish the significance, at the 10% level, of the difference between the HPDV and STT means of the geochemical reference materials PACS-1, MESS-2, BSK-1, AGV-1 and JB-1a.

Element	PACS-1 d.f. = 4 t_{crit} = -2.132 and 2.132	MESS-2 d.f. = 4 t_{crit} = -2.132 and 2.132	BSK-1 d.f. = 2 t_{crit} = -2.920 and 2.920	AGV-1 d.f. = 2 t_{crit} = -2.920 and 2.920	JB-1a d.f. = 2 t_{crit} = -2.920 and 2.920
Li	-1.365	-1.133	-5.632	-6.062	-5.412
Rb	-1.482	-13.427	-5.867	-3.343	-6.458
Sr	1.800	-7.283	-3.080	-21.957	-2.919
Y	6.823	12.073	0.345	-2.009	-5.380
Zr	6.208	13.627	9.984	-4.787	0.229
Nb	2.960	5.880	0.270	0.121	1.807
Mo	3.002	1.621	-2.447	-0.053	0.341
Cs	2.740	-5.450	-2.049	-8.372	-0.780
Ba	3.451	-4.403	-6.723	-13.669	-19.217
La	-1.053	-1.899	-2.038	-3.639	-0.120
Ce	0.096	-1.365	-2.053	-4.006	0.789
Pr	0.880	-1.016	-2.380	-4.168	0.987
Nd	1.089	-0.429	-2.119	-2.212	-0.818
Sm	2.625	-0.189	-1.304	-1.736	-1.154
Eu	1.121	-0.716	-2.147	-0.479	-0.703
Gd	1.220	0.809	-1.382	0.509	-0.150
Tb	1.930	1.973	0.250	2.661	0.122
Dy	5.513	4.100	-0.192	3.475	0.033
Ho	5.649	3.296	0.881	0.573	1.108
Er	3.855	5.883	0.621	0.185	1.600
Tm	3.845	6.578	0.744	0.000	1.623
Yb	12.364	2.523	1.484	0.412	-0.969
Lu	4.824	3.805	1.523	-0.318	0.785
Hf	4.022	9.276	11.331	-0.456	0.133
Ta	2.209	4.115	-0.230	4.025	1.665
Tl	3.008	1.625	0.307	-1.068	1.486
Pb	2.081	0.981	-1.426	1.616	1.261
Bi	1.349	3.012	0.521	1.767	-0.600
Th	1.363	-0.644	-1.276	-8.439	0.194
U	4.107	2.695	-0.781	1.068	0.972

d.f. = degrees of freedom = 4 for PACS-1 and MESS-2; 2 for BSK-1, AGV-1 and JB-1a.

The table also shows that there are certain elements that were indicated to have significant differences between the method statistical means. For PACS-1, with d.f. = 4, α = 10%, and $t_{critical}$ = 2.132, the calculated t statistic was greater than the table value of t ($t > t_{critical}$) for 17 elements, among which are Y (6.823), Zr (6.208), Nb (2.960), the HREEs (3.845 to 12.364), Hf (4.022), Ta (2.209) and U (4.107). For MESS-2, with d.f. = 4, α = 10%, and $t_{critical}$ = 2.132, the calculated t statistic was greater than the table value of t ($t > t_{critical}$) for 13 elements, among which are Y (12.073), Zr (13.627), Nb (5.880), the HREEs (2.523 to 6.578), Hf (9.276), Ta (4.115) and U (2.695). For BSK-1, with d.f. = 2, α = 10%, and $t_{critical}$ = 2.920, the calculated t statistic was greater than the table value of t ($t > t_{critical}$) for Zr (9.984) and Hf (11.331). The results demonstrate an advantage of the HPDV over the STT for the marine sediment GRMs; specifically, there was higher Zr and Hf values, with or without higher HREEs, Y, Nb, Ta and U in the HPDV than in the STT. The difference between the means of the methods was significant.

For the igneous geochemical reference materials, the HPDV results did not show an advantage over those from STT, except for the granite G-2. This was supported by the t-test results for JB-1a and AGV-1, with d.f. = 2, α = 10%, and $t_{critical}$ = 2.920. For JB-1a, $t < t_{critical}$ for Zr (0.229), Hf (0.133) and HREEs (0.033 to 1.623). For AGV-1, the HREEs gave calculated t from 0.000 to 0.573. Only Dy and Ta gave $t > t_{critical}$, Dy with 3.475 and Ta, 4.025. Except for PACS-1, four reference materials shown in Table 3.2 gave an indication that the HPDV results were significantly less than what the STT gave. This was true for elements such as Rb, Sr and Ba. This indicates that the HPDV is less efficient for certain sample matrices than for others.

The data are presented differently to examine the GRMs individually and in more detail. In geochemical studies, the construction of REE plots or extended REE diagrams (spidergrams) is used to evaluate the internal consistency of rare-earth element data, capitalizing on these elements' similarity in chemical characteristics (ionic radii and 3+ oxidation states, with the exception of Ce [4+] and Eu [2+]). Element data are normalized to a reference set of values, *e.g.*, chondrite, or primitive mantle, or shale, to discern trends in the evolution of rock units represented by the sample under study. Chondrite-normalized plots were constructed here to show similarities, or differences, in the results from the usual digestion method which utilizes the screw top teflon vessels and the technique using the high pressure digestion vessels. Chondrite values used to normalize the data obtained in this study were from Table 11.1 of Taylor and McLennan (1985).

It is more clear in these diagrams that there are higher values for Y, Zr, Nb, Hf and the heavy rare-earth elements (HREEs) for the geochemical reference materials PACS-1 (Fig. 3.3a) and MESS-2 (Fig. 3.3b) and higher Zr and Hf for BSK-1 (Fig. 3.3c) when digested through the HPDV. For BSK-1, the light rare-earth elements (LREEs) appear to be slightly lower, however, when processed through the high pressure method. Rubidium is low in this method as well as shown for MESS-2 and BSK-1. Rubidium in BSK-1 using the high pressure vessel averages 58 ± 11 (mean ± 1 standard deviation for 2 replicates, in ppm) compared to 102.46 ± 0.14 (mean ± 1 standard deviation for 2 replicates, in ppm)

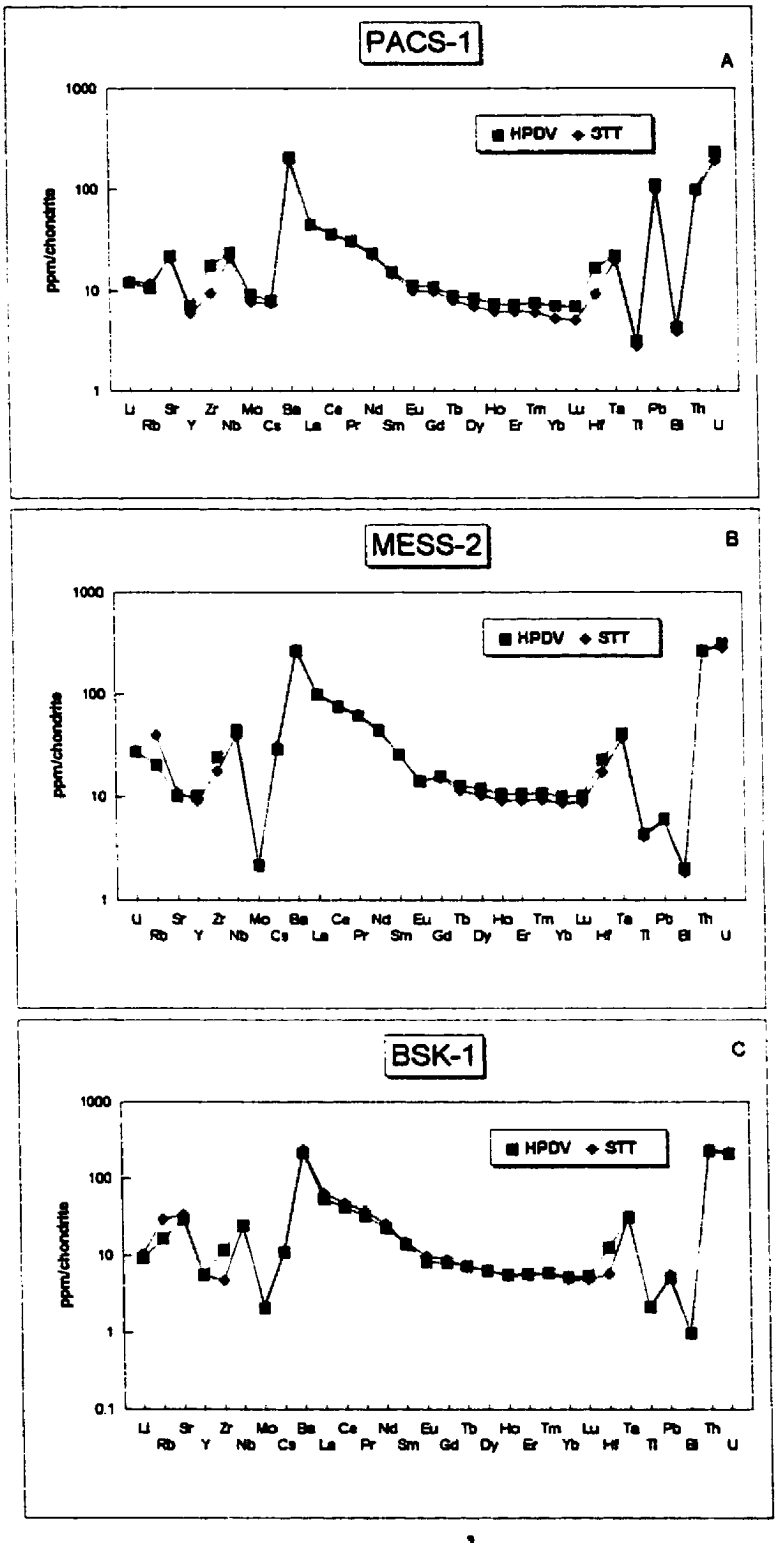

Fig. 3.3. Chondrite-normalized plots for (a) PACS-1, (b) MESS-2 and (c) BSK-1 showing elevation of Y, Zr, Nb, HREEs and Hf in the HPDV compared with the STT, suggesting better recovery of these elements.

for the screw top teflon. From the MUN database of ICP-MS results (particularly from previous ICP-MS trace runs, numbered 241 to 509), 15 analyses of BSK-1 showed a mean of 76 ppm ± 29 ppm (mean ± 1 standard deviation); a median of 93 ppm; and a minimum of 20 ppm and a maximum of 102 ppm. There appears to be a wide variation in this element's reported concentration during those previous runs. Rubidium was one of 9 elements with lesser precision (3 to 7% RSD) whose behaviour, together with Cs, was attributed to sensitivity to reagent and environmental contamination during the early stages of ICP-MS developmental work at MUN (Jenner *et al.*, 1990). It is possible that such is also the case here with some of the GRMs in the present study. Recent compilation by Tubrett *et al.* (1997), however, shows very good agreement for Rb between ICP-MS solution results (using STT as the digestion technique) and results from XRF. It is not clear why Rb behaved this way in the present study, using the HPDV as the digestion procedure.

To show the size of the relative differences in the HPDV and STT results for the sediment reference materials, they are presented in another way in Fig. 3.4a, b , c. Zirconium values are higher by about 40%, 90% and 150% for MESS-2, PACS-1 and BSK-1, respectively. Hafnium values are elevated by approximately 35%, 80% and 120% for these same GRMs. Yttrium values are higher by about 20% and 10% in PACS-1 and MESS-2, respectively; while Nb values are greater by about 10% for both GRMs. The heavy rare-earth elements are higher by approximately 20% compared with the values obtained using

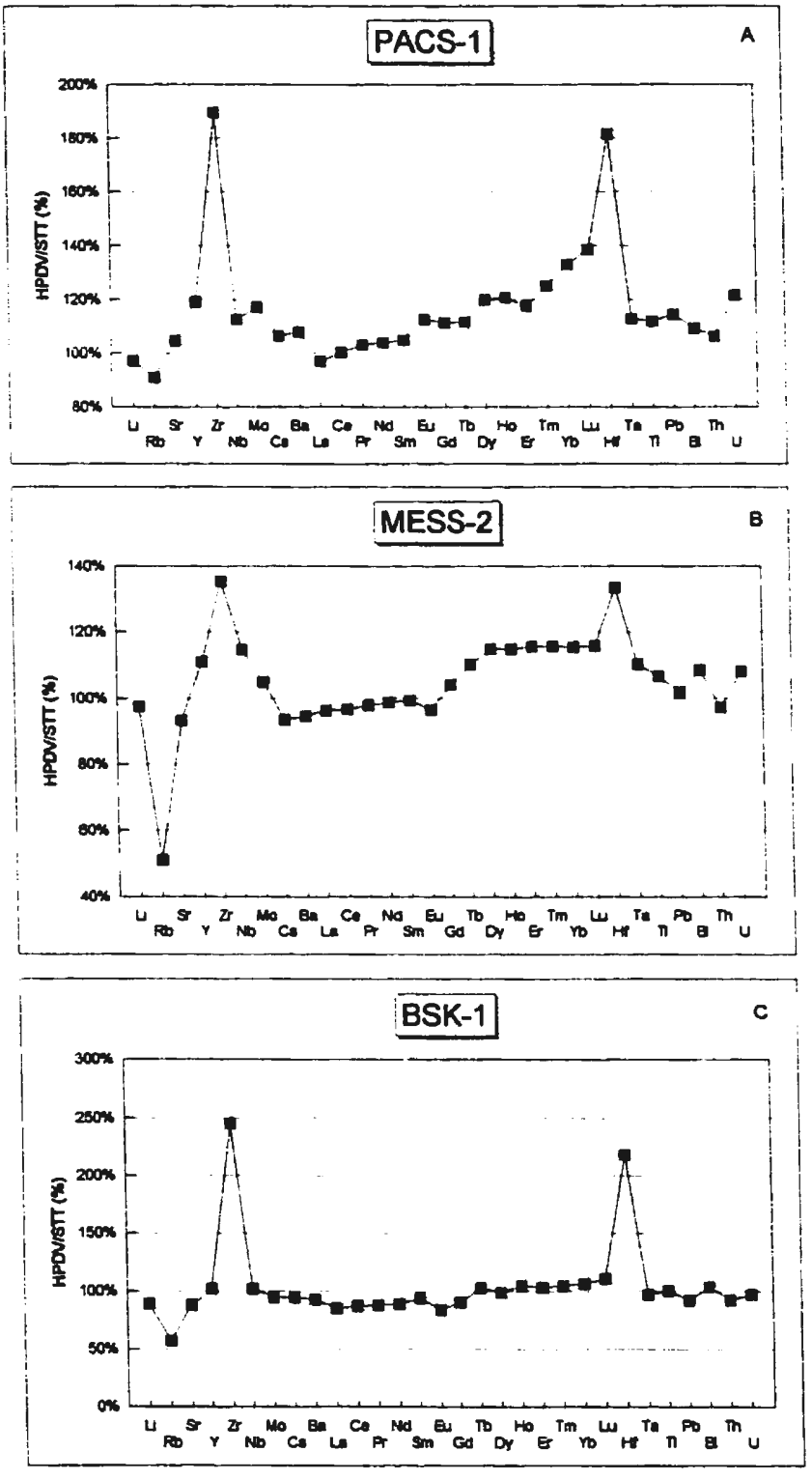

Fig. 3.4. Ratio of HPDV values with respect to the STT values for PACS-1, MESS-2 and BSK-1, showing higher Zr and Hf, generally with higher HREEs.

the STT. Uranium was 10% higher in MESS-2 and 20% higher in PACS-1 when the HPDV was used. The results demonstrate more complete decomposition of heavy minerals incorporated in the marine sediment GRMs using the high pressure method. Heavy minerals are expected to accumulate in marine depositional environments, and as such, the respective sources of these materials and are likely to partition into the clay-sized fraction of the sediments. The correspondence of increased Zr, Hf, HREEs and U in PACS-1 and MESS-2 (and Zr and Hf for BSK-1) from the high pressure vessels is most probably a manifestation of effective decomposition of zircon and garnet as these silicate minerals feature extreme enrichment of heavy rare-earth elements compared with other typical heavy minerals (Taylor and McLennan, 1985).

The chondrite-normalized plots essentially show no difference between the methods for the andesite and basalt GRMs (AGV-1, BCR-2, JB-1a, NBS-688) (Fig. 3.5 to Fig. 3.8). Thallium, Pb and Bi values are elevated for NBS-688 from the high pressure vessels although the values are toward the low end, and Tl and Bi are approaching their respective detection limits. The Zr, Hf and HREE elevation exhibited in the sediment GRMs is not displayed in these volcanic rock reference materials. Rubidium in AGV-1 is about 25% lower in the HPDV compared with the value obtained from the STT. This lower Rb value from HPDV in an andesite rock, together with similar behaviour in the marine sediment materials, indicates that this "loss" of Rb may be due to some other reason than one related to sample matrix. This probably points to a procedural cause but besides a review of the method under study, the matter has not been investigated further.

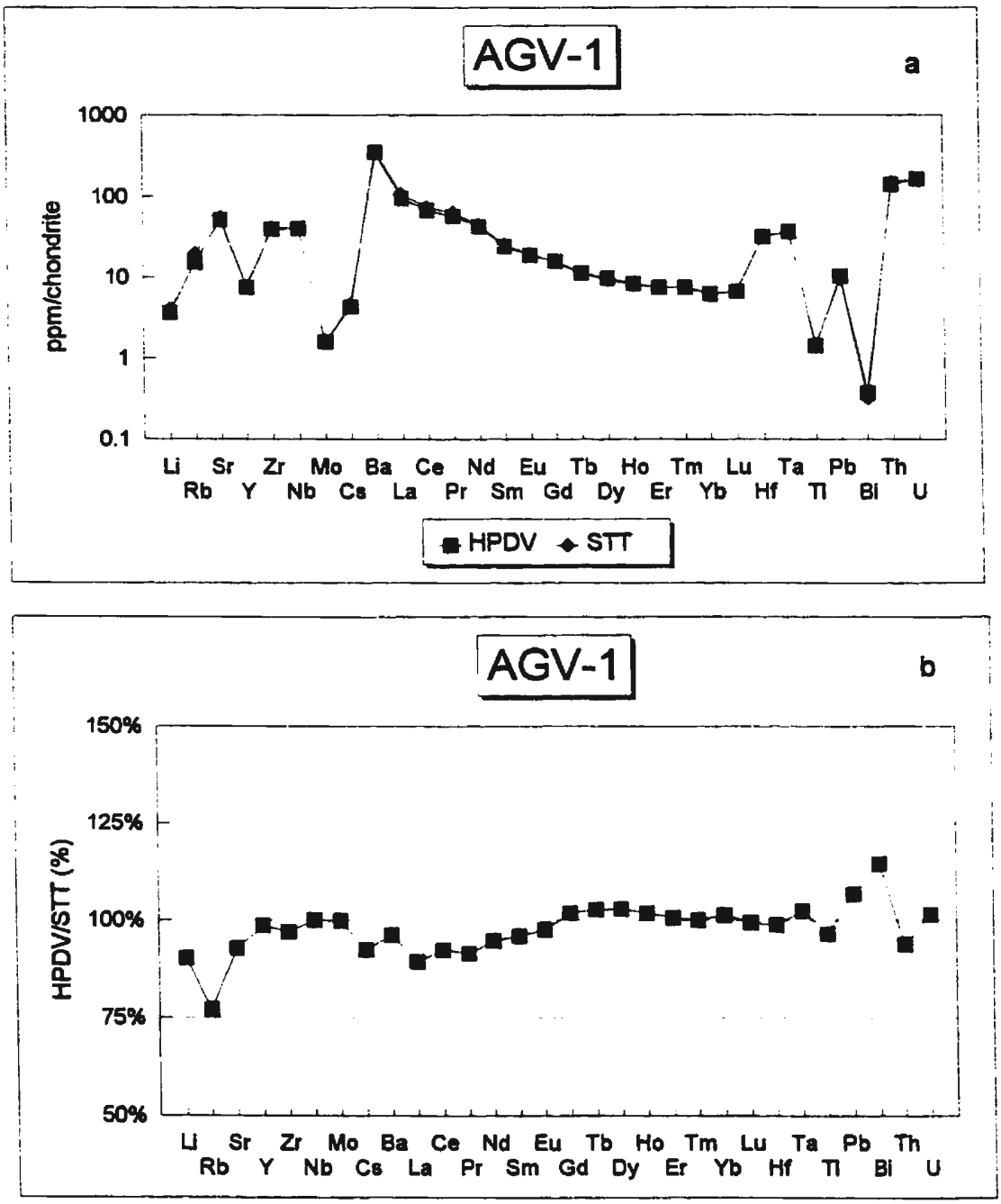

Fig. 3.5. Results for AGV-1 using HPDV compared with those using STT, shown as (a) chondrite-normalized plot, and (b) as the ratio (HPDV/STT).

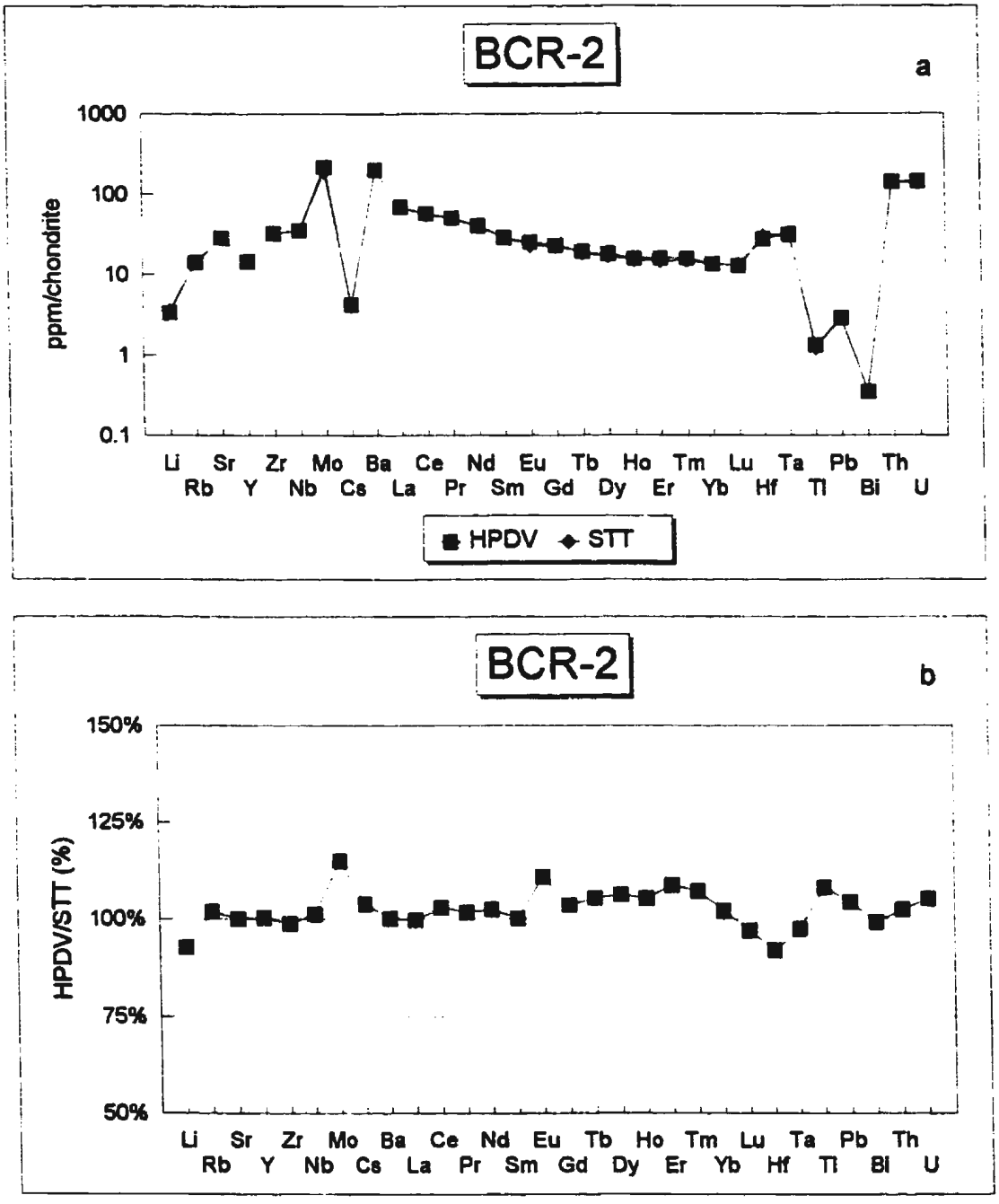

Fig. 3.6. Results for BCR-2 using HPDV compared with those using STT, shown as (a) chondrite-normalized plot, and (b) as the ratio (HPDV/STT).

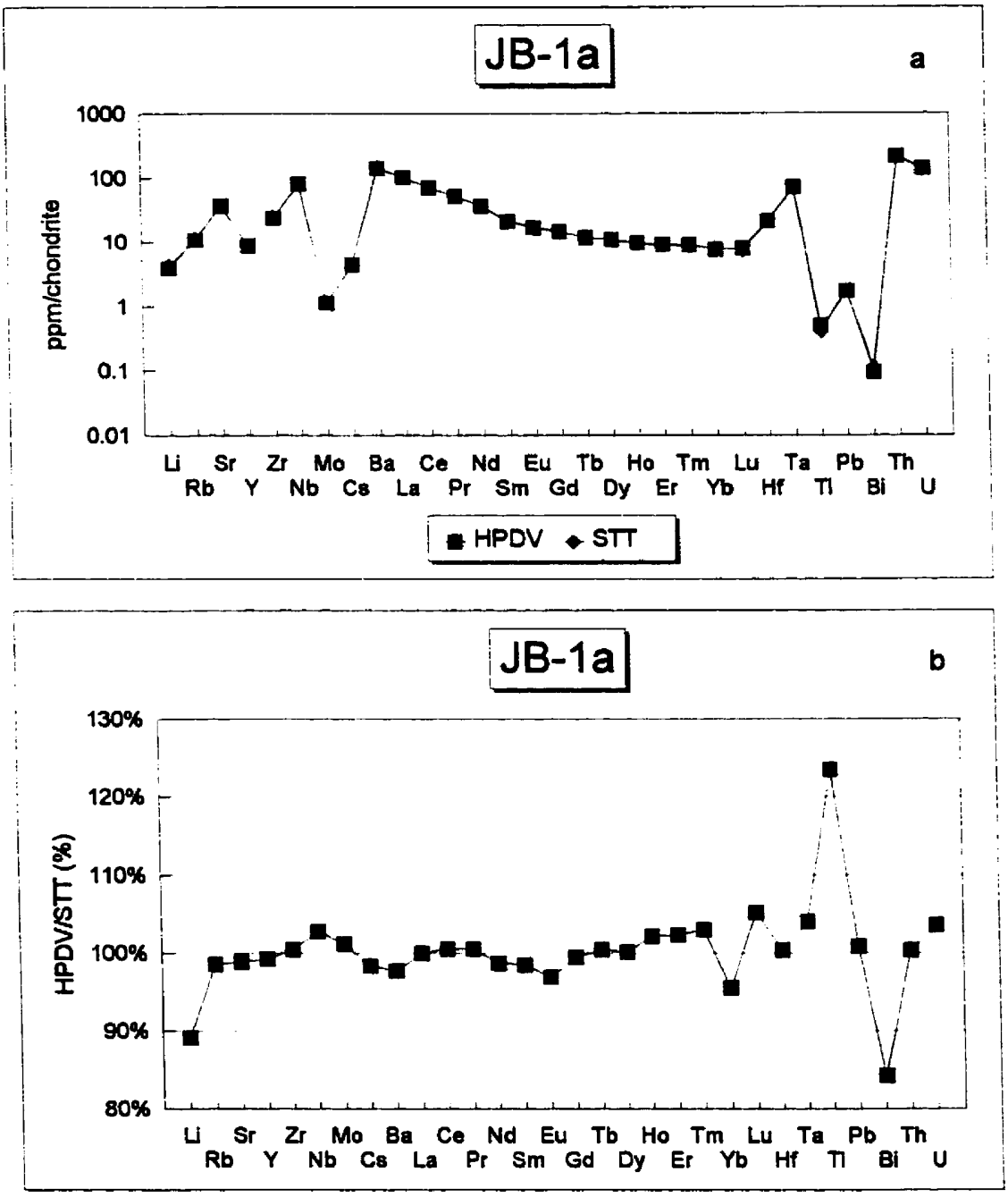

Fig. 3.7. Results for JB-1a using HPDV compared with those using STT, shown as (a) chondrite-normalized plot, and (b) as the ratio (HPDV/STT).

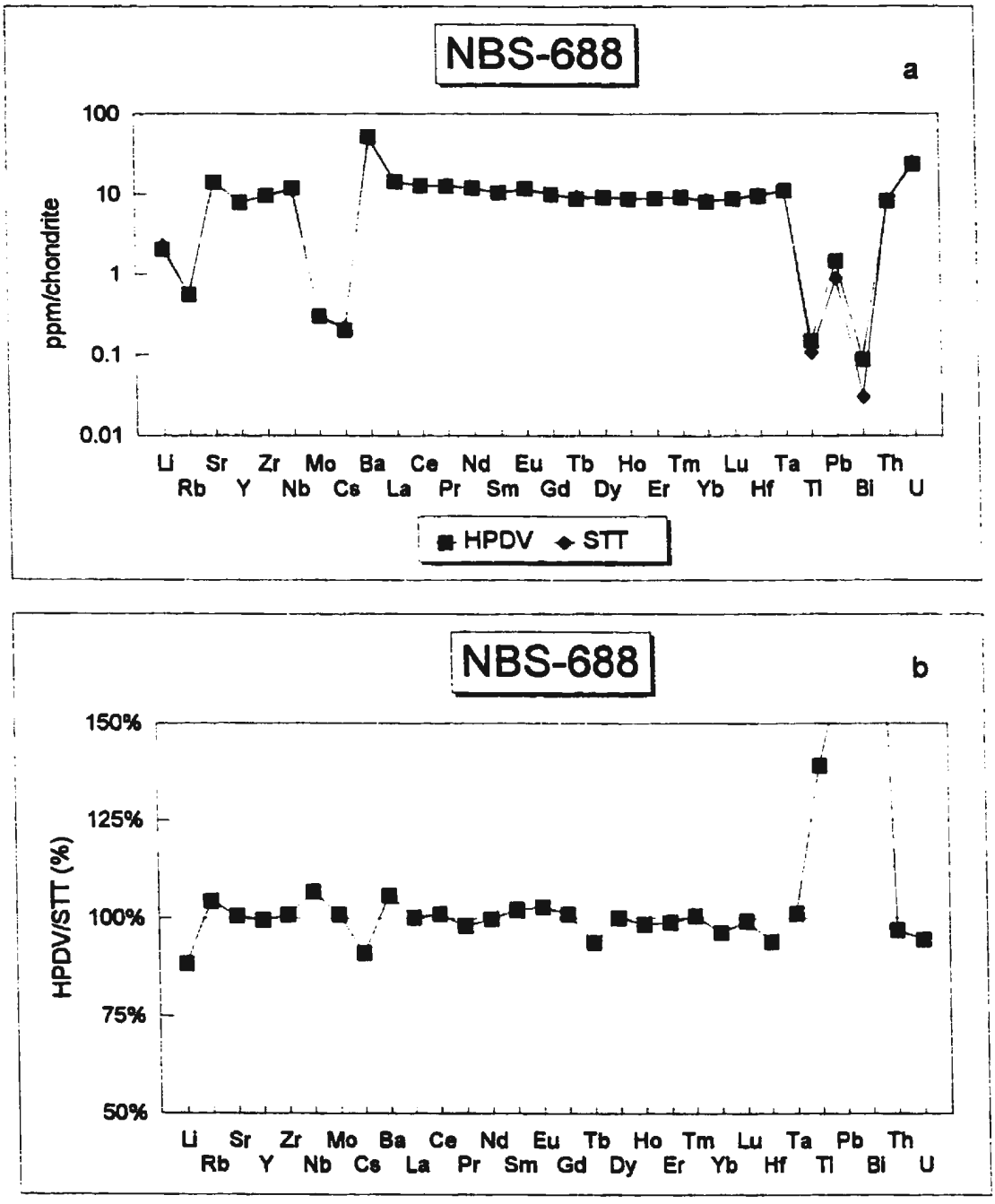

Fig. 3.8. Results for NBS-688 using HPDV compared with those using STT, shown as (a) chondrite-normalized plot, and (b) as the ratio (HPDV/STT).

No significant difference between the two digestion methods is indicated in the results for DNC-1, MRG-1, SY-2 and SY-3 (Fig. 3.9 to Fig. 3.12). It should be noted that the observations made here are based not on replicate analyses but only on one digestion for each of these GRMs. There is a higher Hf value for DNC-1 from the HPDV compared with that from STT (1.2 ppm vs 1.0 ppm). The mean of Hf values from MUN ICP-MS trace runs 241-509 is 1.05 ppm but the maximum of the 32 measurements in these runs reaches 1.42 ppm. DNC-1 values from the HPDV compares well with the averages of 11 analyses from Jenner *et al.* (1990) and the compiled values from Gladney and Roelandts (1988) and Govindaraju (1989). The slight difference in Tl values from HPDV and STT is not significant as both are near the detection limit. The mean for Tl in the MUN compilation is 0.05 ppm which also approaches detection limits. For MRG-1, there is a suggestion of elevated HREEs and hafnium in the HPDV. Bismuth exhibits a 900% difference (0.930 ppm vs 0.103 ppm) but MUN ICP-MS trace runs 510-633 show that this element has not given a precise value for this GRM historically as exemplified in the work of Toms (1996). These previous trace runs have a bismuth value of 0.3 ppm ± 0.7 ppm. Uranium by HPDV in MRG-1 was 60% of the STT average (0.3 ppm vs. 0.5 ppm); however, the STT average has a standard deviation of 0.2 ppm. The syenite reference materials SY-2 and SY-3 gave very similar results for both STT and HPDV with Mo a little higher (20-25%) in the high pressure vessels. However, the Mo value in the HPDV still falls within the respective range of values generated for SY-2 and SY-3 in MUN ICP-MS trace runs 241-509. Tantalum gave a lower value by about 25% in the HPDV for SY-3 (18 ppm) which is even below the range obtained for the GRM in MUN ICP-MS trace

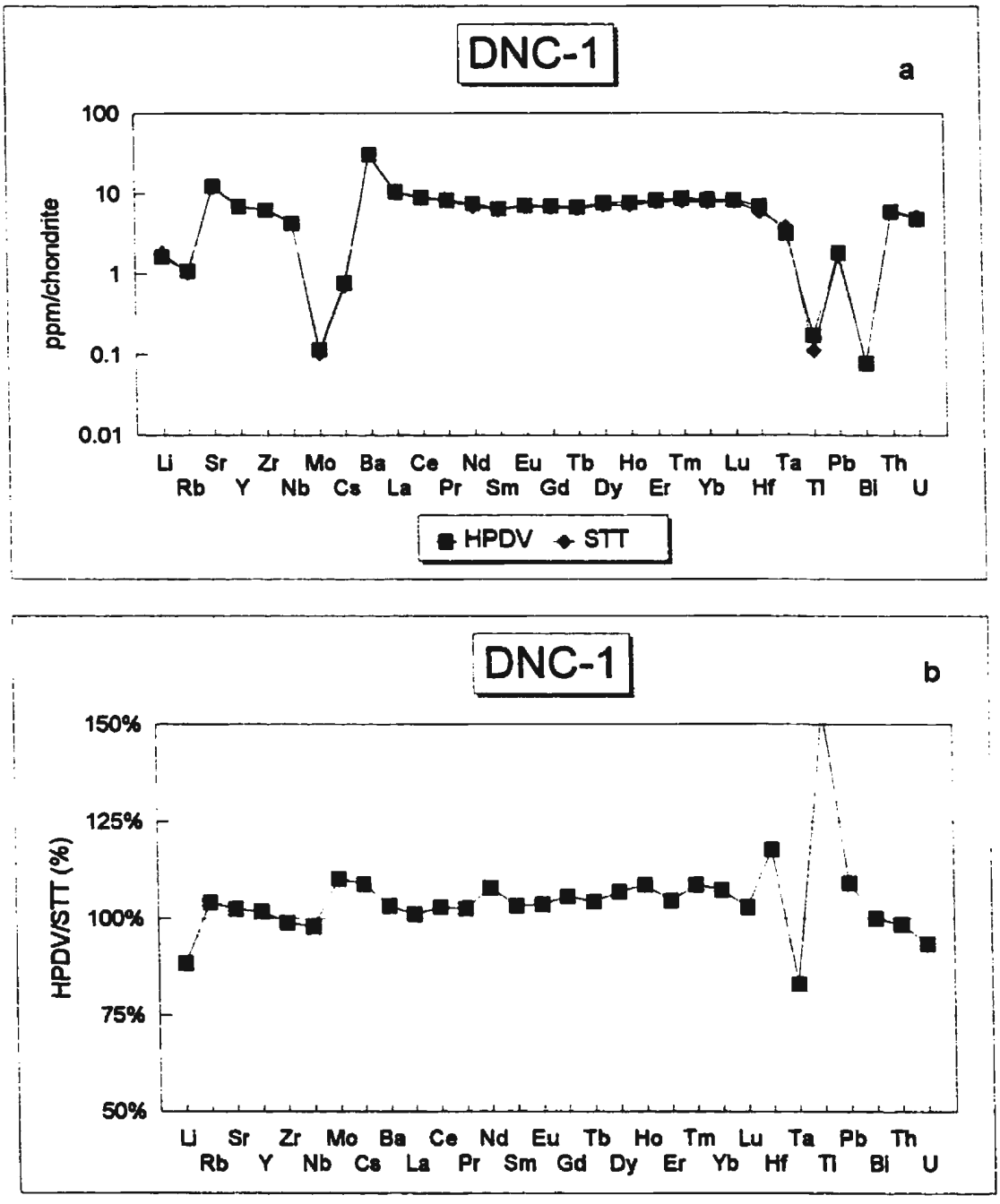

Fig. 3.9. Results for DNC-1 using HPDV compared with those using STT, shown as (a) chondrite-normalized plot, and (b) as the ratio (HPDV/STT).

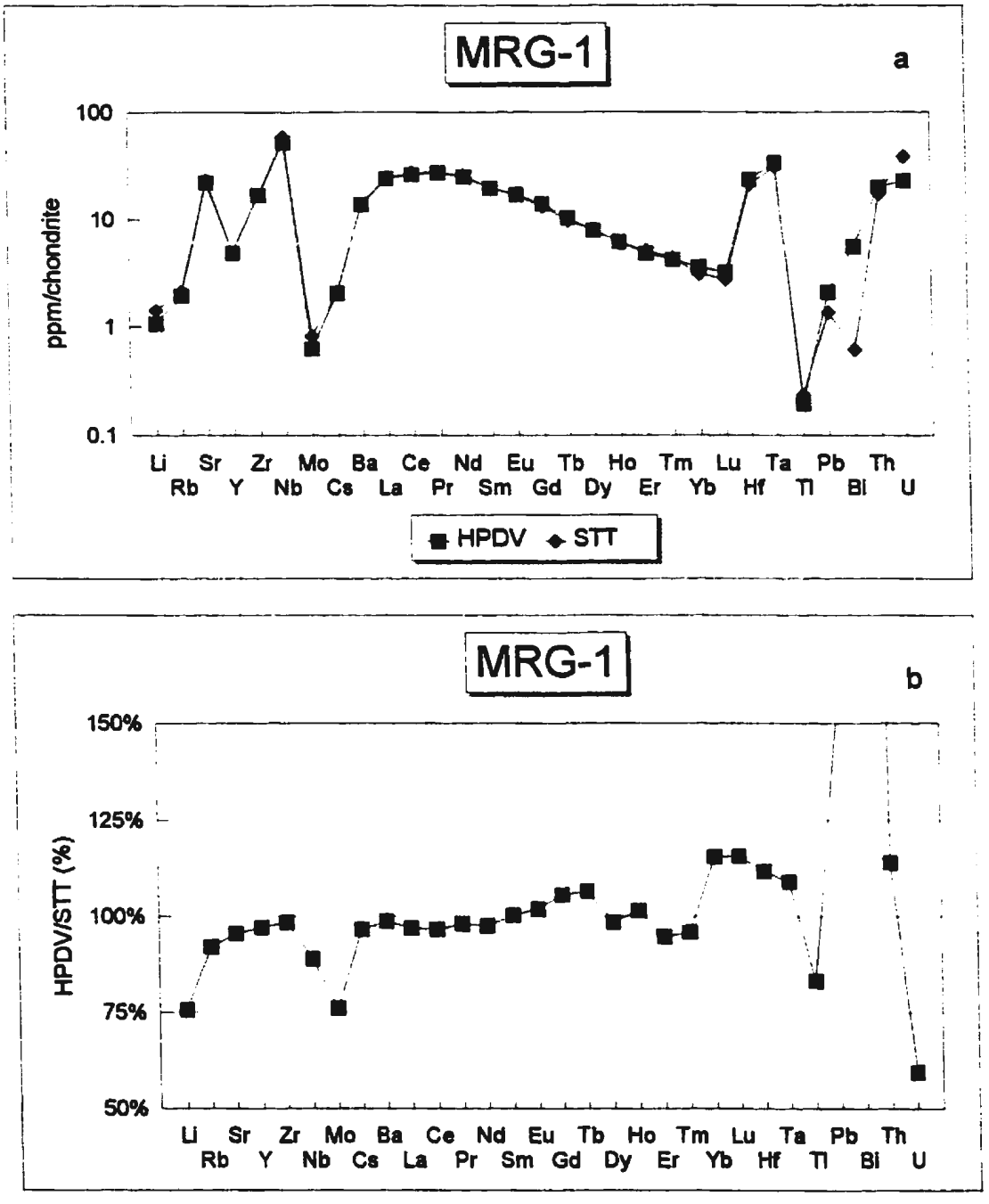

Fig. 3.10. Results for MRG-1 using HPDV compared with those using STT, shown as (a) chondrite-normalized plot, and (b) as the ratio (HPDV/STT).

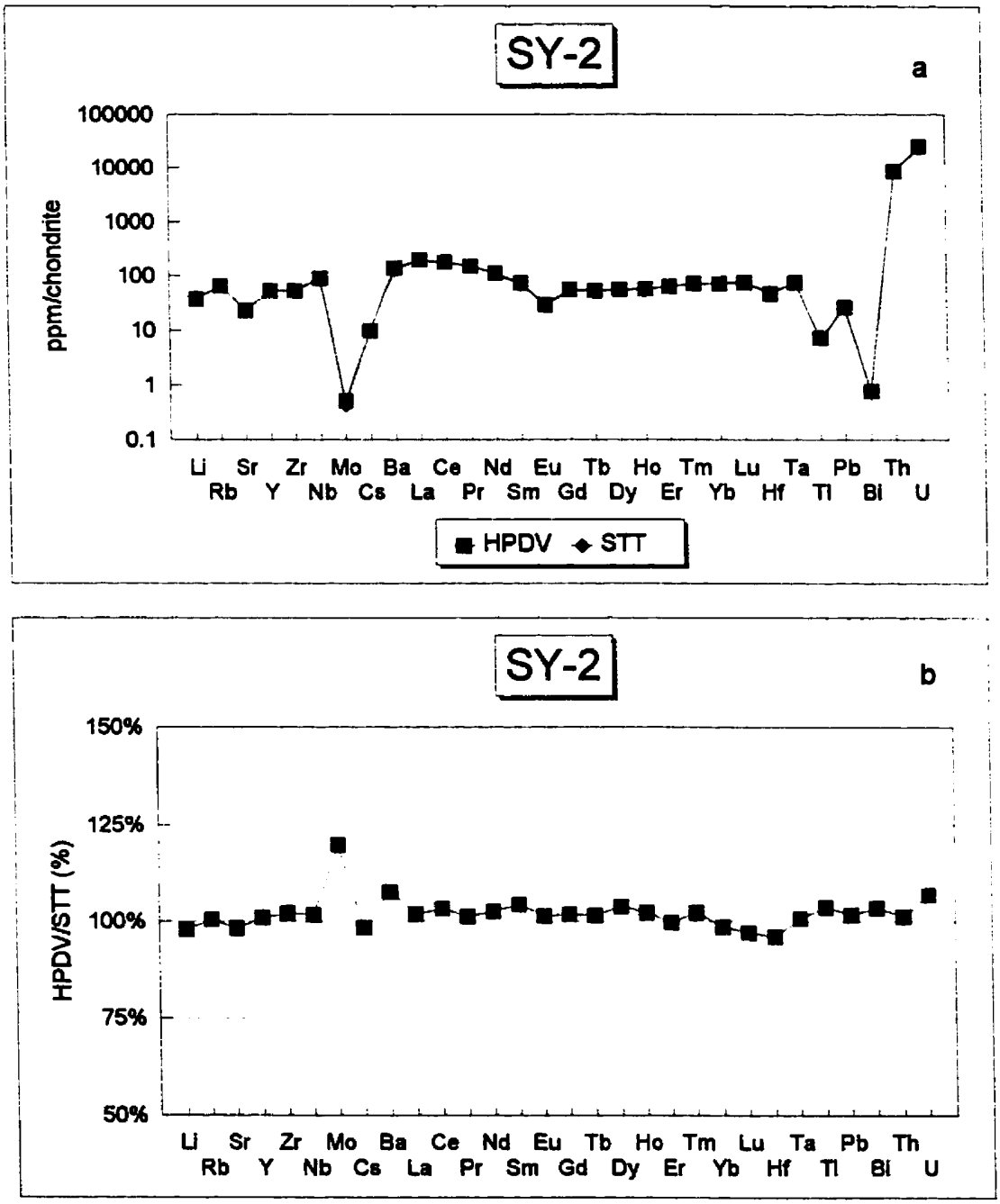

Fig. 3.11. Results for SY-2 using HPDV compared with those using STT, shown as (a) chondrite-normalized plot, and (b) as the ratio (HPDV/STT).

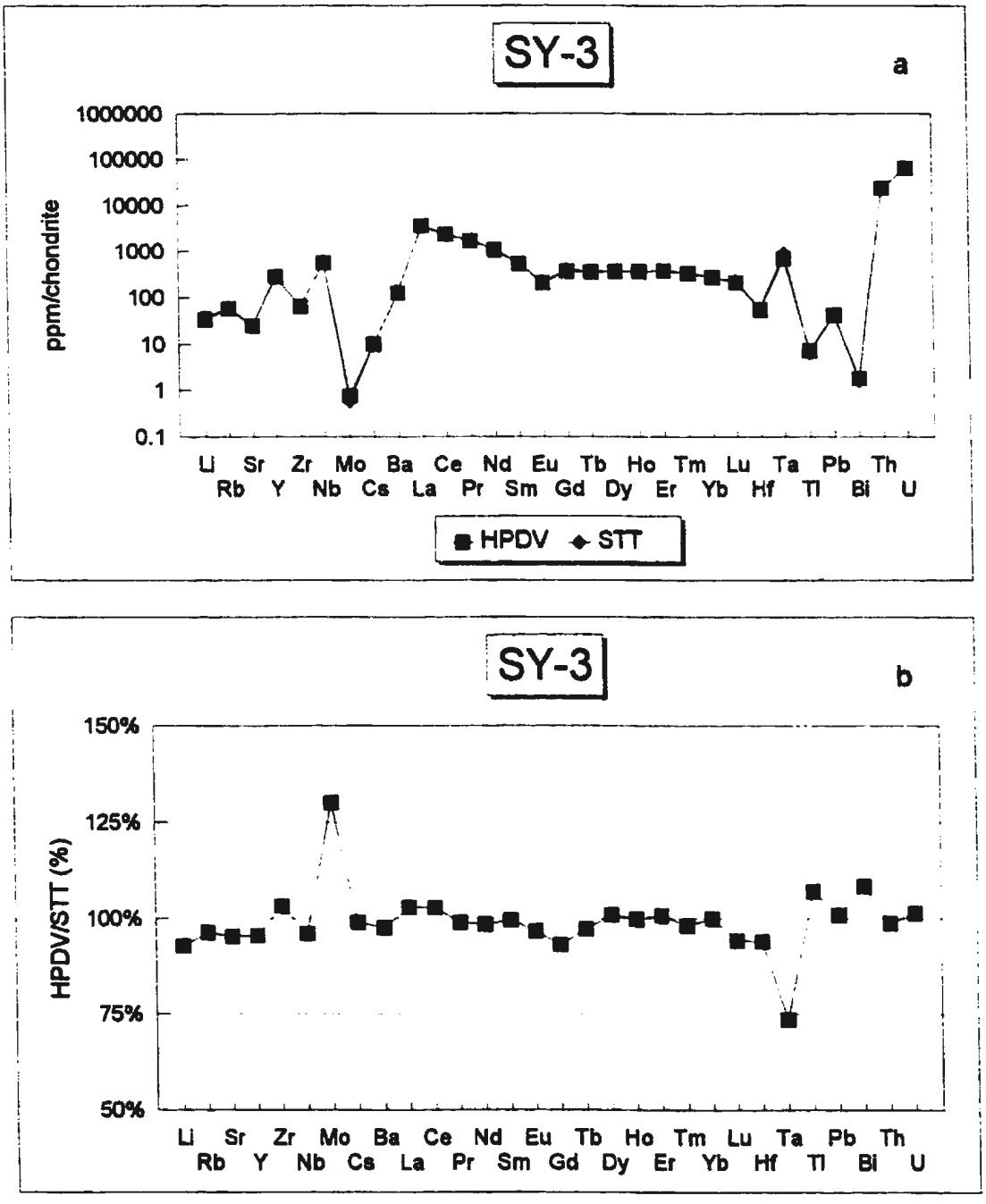

Fig. 3.12. Results for SY-3 using HPDV compared with those using STT, shown as (a) chondrite-normalized plot, and (b) as the ratio (HPDV/STT).

runs 241-509. Together with Nb, the poor precision of Ta is thought to result from memory effects and/or solution instability (Jenner *et al.*, 1990). For Nb, memory effects due to material deposited on and later eroded off the sample interface and skimmer of the ICP-MS have been documented (Longerich *et al.*, 1986). They showed that Nb and Zr stayed in the system up to 60 min from introduction. Rubidium, Sr and Y were quick to clear the system, while Mo cleared after an hour although it was slow in doing so. Other portions of the ICP-MS where previous sample material may remain are the tubing, nebulizer, spray chamber and torch. This can cause significant signal enhancements and is therefore an important reason why sufficient wash or flush times are incorporated in the MUN ICP-MS analytical programs.

The granite reference material G-2 gave results that are somewhat different from those of the other GRMs; although, again the HPDV result is only from a single digestion. The extended REE plot shows clearly that values for most elements are lower when the high pressure vessel is used (Fig. 3.13a). The rare-earth elements are from 50 to 75% lower in the HPDV, however, there is still some suggestion of HREE elevation relative to the LREEs (Fig. 3.13b) compared to corresponding values in the STT. This could not be due to the rudimentary difference in matrix type of the granite G-2 compared with the other GRMs since the syenites SY-2 and SY-3 showed remarkable agreement between the 2 digestion methods. Although it is one of the more "evolved" rock types among the materials studied, it should not be a factor in the apparent "loss" of element responses when the HPDV is used. On the contrary, the relative enrichment in the granites and the

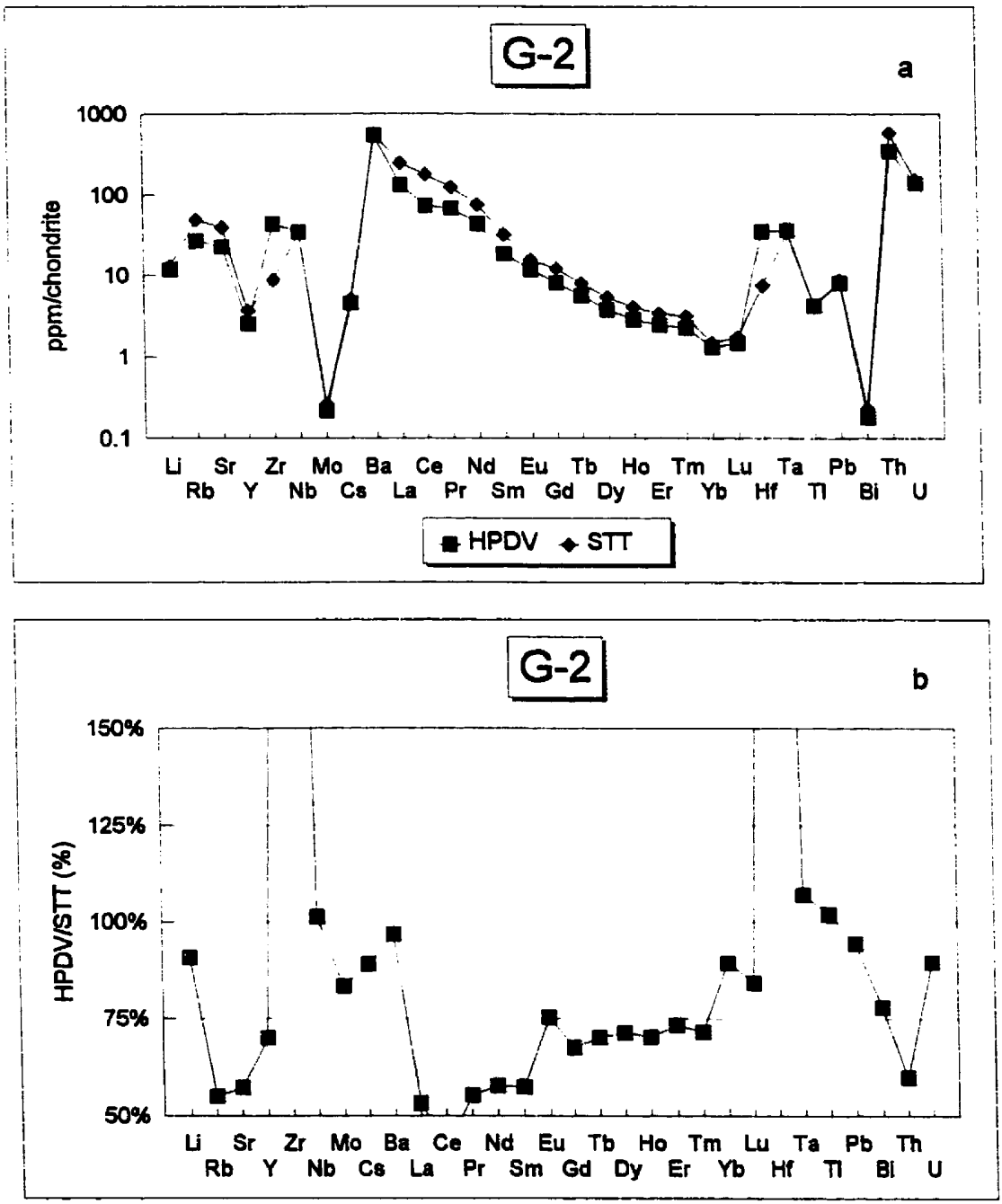

Fig. 3.13. Results for G-2 using HPDV compared with those using STT, shown as (a) chondrite-normaliilzed plot, and (b) as the ratio (HPDV/STT).

syenites should aid in better recovery of values when the high pressure closed vessel is employed. However, it would be best to explore further once more analyses of G-2 are done in order to corroborate these results. The results from the only 2 analyses of this reference material included in MUN ICP-MS trace runs 510 -633 showed RSDs from 16% to 35% for the elements Rb through Pb. The discrepancy shown, although large, may be due to analytical variation and can thus be substantiated by additional analyses.

Nevertheless, one observation that stands out is the very striking enrichment of Zr and Hf which are nearly 500% higher in the HPDV than in the STT. The HPDV results for these elements are 240 ppm and 6 ppm, respectively; while the STT results gave a mean of 49 ppm and 1.4 ppm, respectively. The mean of 2 analyses in MUN ICP-MS trace runs 510-633 is 44 ppm for Zr and 1.2 ppm for Hf, or close to what the STT indicated. As in the sediment GRMs, this demonstrates a more complete decomposition of resistant minerals. For a granite, these are most likely zircons and garnets occurring as accessory minerals in the rock. The effect of analytical variation notwithstanding, the HPDV is indicated to be more efficient in dissolving hard-to-decompose minerals than the STT even for this reference material.

From the foregoing discussion, it can be concluded that the use of the HPDV proved more successful in dissolving resistant minerals in the marine sediment and granite reference materials than the standard STT method used at MUN as indicated by higher values for Zr and Hf, with or without corresponding high values for Y, Nb, HREEs and U. Zirconium

was 40% to 150% higher when the HPDV was used; while Hf was 35% to 120% higher compared to when the STT was used. The HREEs were generally 20% higher in the HPDV; while Y, Nb and U were 10% to 20% higher. The HPDV did not show an advantage over the STT, however, for the other igneous rock reference materials. These results demonstrate that the HPDV was more efficient for certain sample matrices than for others.

3.4.2. High Pressure Digestion Vessel and X-ray Fluorescence Spectrometry

X-ray fluorescence spectrometry affords a set of values that may be used to evaluate the completeness of dissolution for the ICP-MS acid digest methods. Being a solid sample method, XRF has no dissolution and solution stability problems that can greatly hinder accurate ICP-MS analysis (Tubrett *et al.*, 1997). The MUN XRF trace protocol uses pressed pellets made from 5.00 g of the sample powder using 0.70 g of a phenolic resin as binder. Data are obtained using a Fisons/ARL (Mississauga, Ontario, Canada) model 8420+ sequential wavelength-dispersive x-ray spectrometer (Longerich, 1995).

Ten elements common to both MUN ICP-MS trace package and MUN XRF trace runs were used here to evaluate further the results from using the high pressure digestion vessels (HPDVs). These elements are Rb, Sr, Y, Zr, Nb, Ba, Ce, Pb, Th and U. Comparison between the 2 methods, *e.g.*, for quality control purposes, is efficiently achieved by examining the results for these elements, especially for Rb, Sr, Y, Zr and Nb,

because of their natural abundance and low detection limit by XRF. A search of the 1996 XRF database at MUN revealed that of the 12 geochemical reference materials, only 6 have been recently analyzed using the XRF trace package. The number of analyses ranged from 46 for SY-2 to 600 for PACS-1, especially since these materials are MUN calibration materials for some analytes. MESS-2 had the smallest number of analyses (4) due to the fact that this reference material was only aqcuired recently.

Figure 3.14 exhibits chondrite-normalized plots for the 6 geochemical reference materials (PACS-1, MESS-2, AGV-1, DNC-1, SY-2, and SY-3) and demonstrates reasonable agreement of the HPDV results with those from XRF, especially for the syenites SY-2 and SY-3. Thorium for PACS-1 gave a mean of 4.2 ppm ± 0.23 ppm (1 standard deviation) while U gave a mean of 2.8 ppm ± 0.1 ppm from 4 analyses using the high pressure vessels. No published value is available for Th in PACS-1 and U was measured by MacLaren *et al.* (1988) at 3.02 ppm ± 0.04 ppm using isotope dilution. The material has mostly given a value below the detection limit for Th and U in MUN XRF trace runs in 1996. Thorium and Ce are both below their respective detection limits for the dolerite reference material DNC-1 in these previous MUN XRF trace runs.

Percentage-wise, the resulting excellent agreement for SY-2 and SY-3 is also shown by the nearly 100% reproduction of XRF results by those from HPDV (Fig. 3.15). The Rb "loss" cited previously is again evident in the Fig. 3.15 plots for PACS-1, MESS-2 and AGV-1. As mentioned earlier, this is generally in contrast to compiled results so far

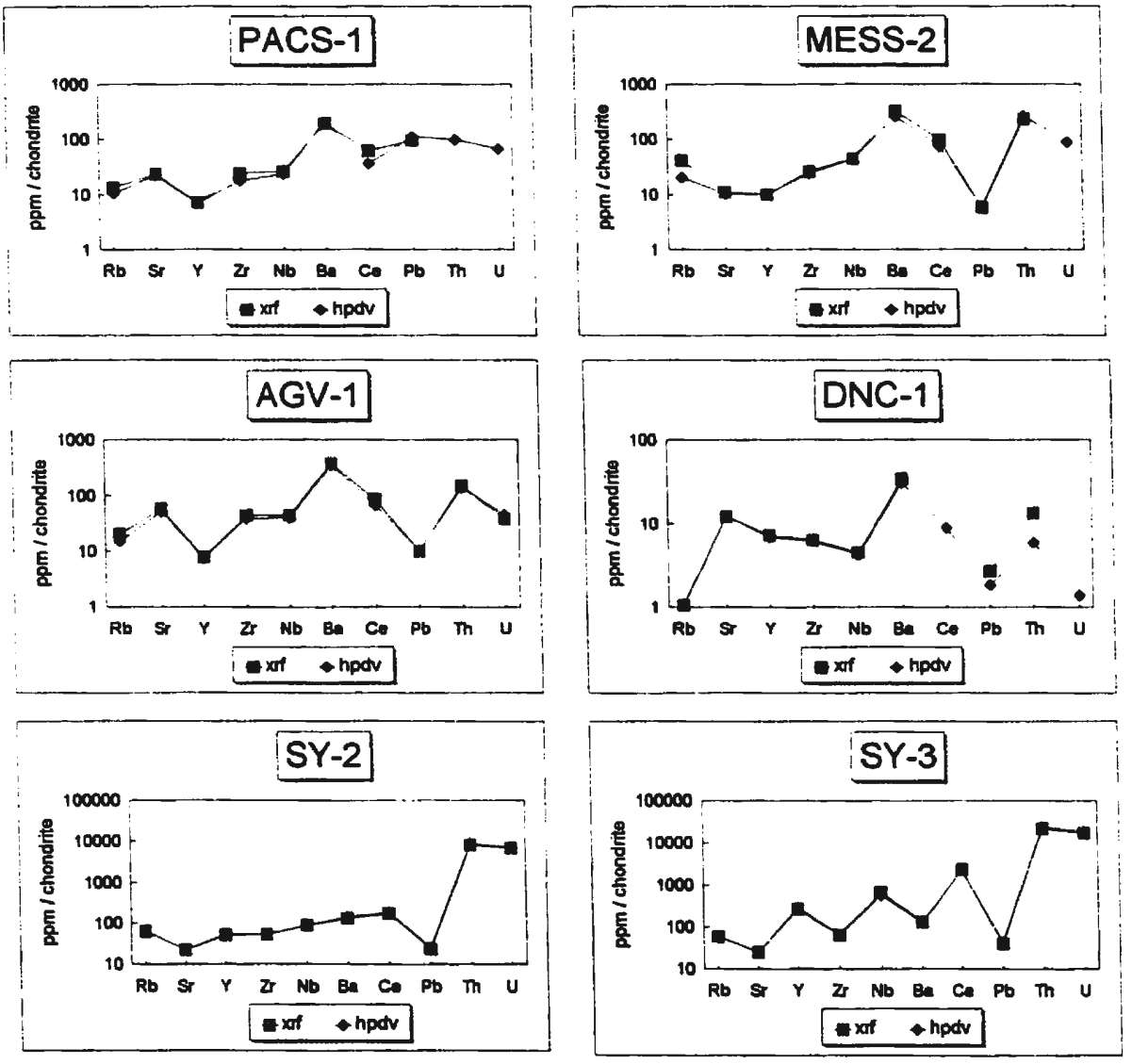

Fig. 3.14. Chondrite-normalized plots for 10 elements in 6 GRMs. Elements are common to ICP-MS trace and XRF trace packages. ICP-MS trace results were from HPDV. Plots show reasonable agreement between HPDV and XRF for Rb, Sr, Y, Zr, Nb, Ba, Ce, Pb, Th and U.

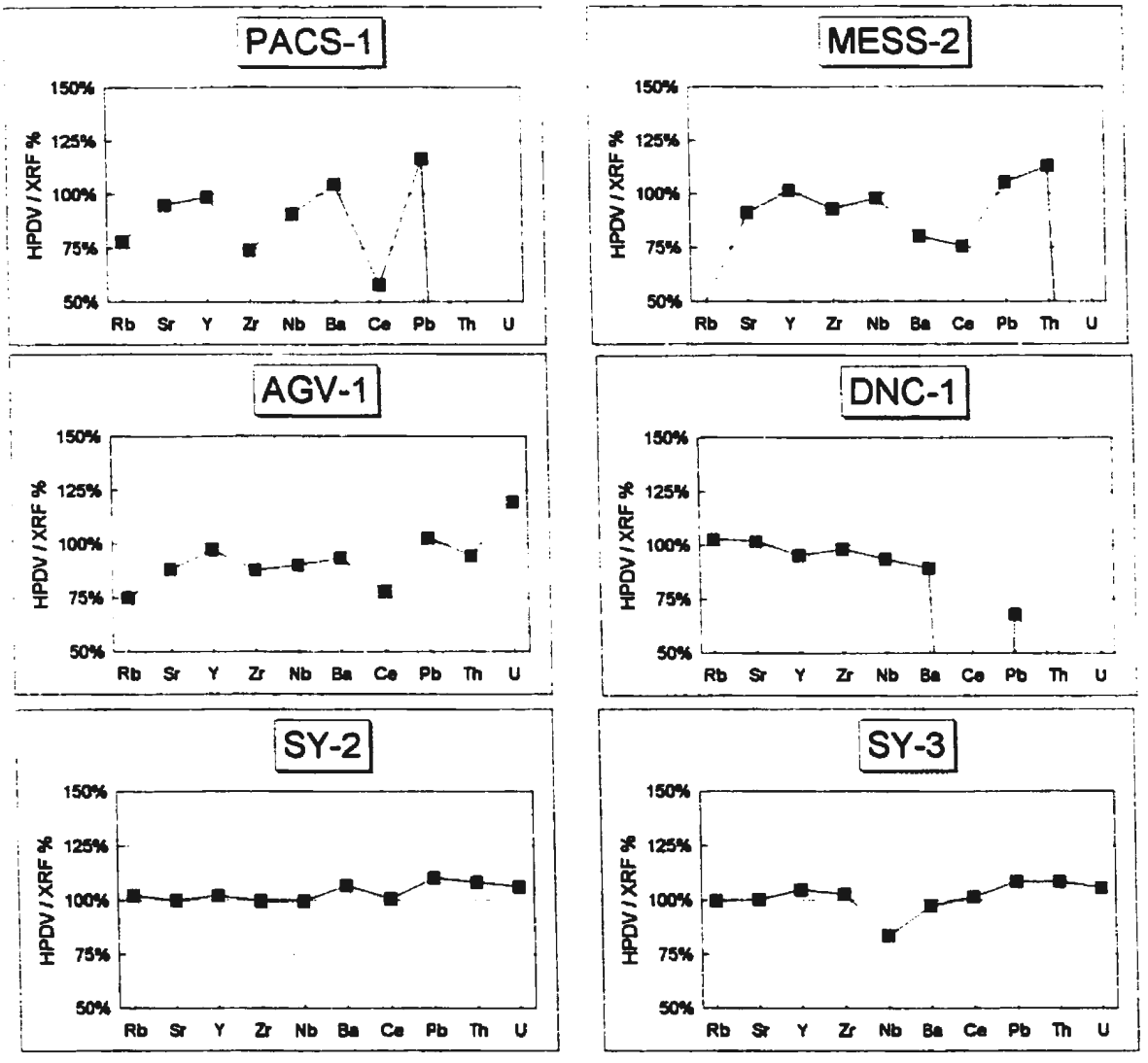

Fig. 3.15. Ratio of HPDV values relative to XRF results for 10 elements in 6 GRMs. Shown are elements which are common to ICP-MS trace and XRF trace packages. Zr is low in PACS-1 using HPDV; Nb is low in 4 of 6 GRMs; Ce is low in 3 of 6 GRMs.

accumulated in this laboratory where there is usually a very good agreement between XRF and ICP-MS results for this element. This good agreement similarly applies to Y, Sr and Ba historically and is reproduced here for Y in all the GRMs highlighted. It is generally shown for Sr and Ba by most of the reference materials except MESS-2 (for Ba) and perhaps AGV-1 (for Sr).

Niobium is low when HPDV was used for 4 out of the 6 GRMs. Due to solution stability problems for this element, XRF is the preferred method for Nb in the MUN laboratory. Cerium was low in 3 of the 6 materials. The advantage of the use of HPDV over the STT in the determination of Zr in sediments, as discussed previously, does not apply for PACS-1 when HPDV is compared with XRF. Lower Zr values in HPDV are also indicated for AGV-1, and MESS-2, but good agreement is shown for DNC-1, SY-2 and SY-3.

Generally, the results for the elements common to both ICP-MS trace and XRF trace (Rb, Sr, Y, Zr, Nb, Ba, Ce, Pb, Th and U) show reasonable agreement for the geochemical reference materials, PACS-1, MESS-2, AGV-1, DNC-1, SY-2, and SY-3. With the XRF results as an indication of completeness of dissolution, the ICP-MS results for the HPDV digest method approximates closely the XRF trace results for the common elements particularly for the syenite reference materials. There remains an indication of incompleteness of digestion of certain minerals as shown by the low bias of Zr values in PACS-1 using HPDV (75% of XRF result). In this case, it appears that the HPDV method may be improved by lengthening the "oven" time during the dissolution stage to about 20

to 24 h. Even so, the total time allotted for this phase is considerably shorter than what is normally used for the STT method. The disadvantage, however, is that the number of samples that can be simultaneously digested is restricted by the number of vessels to an assembly (6). Although there are 3 assemblies presently (18 samples altogether), the STT can easily and inexpensively accommodate a batch that is 3 to 4-fold as much.

3.5. Summary and Conclusion

Acid digestion of geological samples is prone to dissolution problems when the samples contain resistant minerals especially zircon. This has been addressed by many workers with the use of high pressure digestion techniques with varying degrees of success. The present study fabricated teflon vessels for high pressure dissolution and examined their effectiveness in the ICP-MS analysis of several geochemical reference materials by comparing results from the standard acid digest method (closed vessel, low pressure) that is routinely employed in the MUN ICP-MS laboratory. Further comparison was made with results from the XRF analysis of the GRMs as a measure of completeness of digestion.

Based on the responses of the various geochemical reference materials when dissolved using the high pressure digestion procedure (HPDV) as compared with the usual method utilizing the screw top teflon (STT), the GRMs can be classified into 3 groups. These 3 groups are respectively based on the following element responses:

1. high Zr and Hf, generally with high Y, Nb, HREEs and U in the HPDV (marine sediments);
2. Generally similar element patterns for HPDV and STT (andesite, basalts, syenites); and
3. low results from HPDV, but with high Zr and Hf (granite).

The first group clearly indicates a more complete dissolution of Zr-bearing minerals in the sediments. The values derived for MESS-2 come close to those obtained from x-ray fluorescence spectrometry; however, those for PACS-1 are still appreciably lower than the XRF counterpart. This could be due to still-undissolved amounts of resistant minerals even though the HPDV showed a marked improvement over the STT in recovering Y, Zr, Nb, HREE, Hf and U values in the sediments. Nevertheless, the results for the sediment GRMs, even for G-2, confirm the usefulness of high pressure HF-HNO_3 digestion in attacking resistant minerals. For G-2, the HPDV values were mostly lower compared with those from STT but the 5-fold increase in Zr and Hf and the relative increase in HREEs suggest potential applicability to rocks rich in accessory minerals such as zircons (acid igneous rocks) or garnets (metamorphic equivalents) or other mineral phases with which hafnium and the heavy rare-earth elements are associated (*e.g.*, fluorite) (Date and Gray, 1985).

The study demonstrated the effectiveness of using the high pressure digestion vessel in recovering Y, Zr, Nb, HREEs and U values in the marine sediment reference materials

compared with the routine acid digest method at MUN. The HPDV, however, did not improve on the STT in recovering these elements in the andesite, basalt, dolerite, gabbro and syenite GRMs, in which case both methods generally giving similar results. The recovery by the high pressure method of values for most elements in the granite reference material was poor compared to the STT. This result was from only one sample solution of G-2 and it is possible that somewhere in the sample preparation itself was the source of the large variation. However, this can only be ascertained when more results are available, therefore, more analyses of this material are needed. Nevertheless, Zr and Hf in G-2 were significantly higher in the HPDV, indicating applicability of the HPDV for samples affected by poor digestion. The results for some elements using the HPDV do not seem to be reliable. The HPDV appeared to lose Rb in the digestion of the marine sediments and some of the volcanic rock GRMs, but not the other igneous rock reference materials. The reason for this was not determined in this study, however, it should be part of future work using the HPDV.

The importance of accurate and precise determination of Zr, Hf, the REEs, together with yttrium and other discriminatory elements to geochemical modeling must be emphasized. Serious discrepancies have been pointed out by Longerich *et al.* (1990) in the results for Y and Zr when digested in the usual STT method. In metal form, both Y and Zr are corrosion resistant and have very high melting points (Lee, 1996). Longerich *et al.* (1986) have shown that signal enhancements due to memory effects are easily produced in ICP-MS for Zr and Nb. These concerns and others, such as matrix effects that can suppress or

enhance element sensitivities, interferences by concomitant elements, or oxide formation brought about by changes in operating conditions, are some areas that are the focus of continuing development of methods in determining elements by solution nebulization ICP-MS at the Department of Earth Sciences, MUN. The sodium peroxide (Na_2O_2) sinter procedure has been shown to give excellent results for Y, the REEs, and Th (Longerich *et al.*, 1990). On the other hand, the present study has shown that the high pressure technique possesses good potential in the determination of Y, Zr, Hf, the REEs, along with most other elements in the trace package, in geological samples that may contain resistant mineral phases, such as zircons, oxides, etc. One improvement in the HPDV technique can be made by extending the oven time from the current 12-16 h to 20-24 h. This would most probably bring results as close to the XRF values as possible and the total digestion time would still be only about 25% of that typically spent for the STT.

Chapter 4

Development of a Data Acquisition and Reduction Procedure for Determining Transition Metals and Other Trace Elements for Environmental and Exploration Studies

4.1 Introduction

Analytical determination of some of the transition metals in geological materials has historically been important because of the metals' impact as tools of industrialization, and of civilization as a whole. More recently, environmental issues have re-focused some attention on the analysis of the transition metals which, together with other elements, are causing increased concern to human health. The link between environmental geochemistry and human and animal health has long been recognized but the matter of efficiently tracking trace elements in the environment ultimately depends on improved laboratory capabilities. Such improvement would also benefit the quest for economic mineral deposits especially for blind targets where discovery might rest on detection of subtle changes in rock geochemistry.

In the continuing development of procedures for trace element determination through solution nebulization ICP-MS at Memorial University, one of the foremost goals is to develop methods for routine analysis covering a wide spectrum of elements using simple preparation techniques (Longerich, 1989b; Longerich *et al.*, 1986, 1990, 1993a, b; Friel *et al.*, 1990; Jenner *et al.*, 1990; Jackson *et al.*, 1990). In this study, the first-row transition

metals and other trace elements were the main focus because of potential application in the analysis of both environmental and exploration samples. In conjunction with the high pressure digestion technique described in the previous chapter, we hoped to establish a new data acquisition/reduction package utilizing solution nebulization ICP-MS. With the MUN XRF trace element package, which has a few transition elements in its acquisition program, it would provide added assurance of quality data for some of these transition metals and not be constrained by the amount of sample available. The data acquisition and data reduction scheme described below is proposed to be called the "exploration/ environmental package".

4.2. Selection of Masses

At the start of this study, 29 masses were selected for acquisition in the proposed package. These were ^{51}V, ^{52}Cr, ^{55}Mn, ^{59}Co, ^{60}Ni, ^{65}Cu, ^{66}Zn, ^{75}As, ^{77}Se, ^{79}Br, ^{98}Mo, ^{107}Ag, ^{111}Cd, ^{118}Sn, ^{121}Sb, ^{125}Te, ^{127}I, ^{139}La, ^{140}Ce, ^{141}Pr, ^{145}Nd, ^{167}Er, ^{169}Tm, ^{175}Lu, ^{183}W, ^{201}Hg, ^{208}Pb, ^{209}Bi and ^{232}Th. The choice of mass was generally based on several considerations: selection of the most abundant isotopes, and minimization of interferences from isobaric overlaps, polyatomic or doubly charged ions (McLaren *et al.*, 1987; Longerich *et al.*, 1990; Jenner *et al.*, 1990). ^{52}Chromium (natural abundance 83.8%) often has significant interference from $^{40}Ar^{12}C$ albeit greater sensitivity, especially in high carbon-containing samples. ^{53}Chromium (natural abundance 9.50%) was also included for samples that may have concentrations of Cr which could be swamped by the potentially high interference

from ArC. The samples intended for analysis in this study were sediments that are principally derived from limestone. As CO_2 is removed during sample digestion, the most important oxide interferences were $^{43}Ca^{16}O$ on ^{59}Co and $^{44}Ca^{16}O$ on ^{60}Ni. Likewise, it was anticipated that other oxides might overlap with 2 other analytes: $^{49}Ti^{16}O$ on ^{65}Cu and $^{50}Ti^{16}O$ on ^{66}Zn as rutile is ubiquitous in most sediments. ^{60}Nickel was chosen in preference to ^{58}Ni to avoid the ^{58}Fe isobaric interference; ^{118}Sn was chosen in preference to ^{120}Sn because it was known to be free from isobaric interference (McLaren *et al.*, 1988).

4.3. Data Acquisition

Samples were digested using the high pressure digestion vessels, as described in the previous chapter (Sec. 3.3.3). Digestion times for the samples were approximately 16 h, usually overnight from 5:00 p.m. until 9:00 a.m. the next day. Most of the geochemical reference materials used in the previous chapter were also used in this portion of the study. The final dilution of rock or sample materials was 1 : 2000 or 0.5 g of rock per Kg of solution. The 0.1 g of rock or sample was dissolved in 60 g of solution (refer to Sec. 3.3.3 for details in the digestion procedure); 5 g of this solution were added to 5 g of blank acid (0.2 N HNO_3). A further dilution of 1 : 2 was made when one part spike solution was pumped into a "Y" connector with 2 parts sample solution (approximately $^1/_3$ ml/min spike mixed with $^2/_3$ ml/min sample) just before the solution reaches the nebulizer of the ICP-MS. The "Y" connector is a 3-way connector made of teflon where the sample

and spike are effectively mixed, giving the final dilution of 0.5 g/Kg as the solution enters the ICP-MS. At about the study's mid-point, the analysis was switched from the SCIEX ELAN® 250 ICP-MS to the VG Plasmaquad® PQII+ "S" ICP-MS unit. When the VG was used, the dilution factor was changed owing to the greater sensitivity of the latter unit. In the VG, 0.2 g of the sample solution (from digesting 0.1 g of sample powder and making up to 60 g solution) was added to 10 g of blank acid (0.2 N HNO_3). Further dilution into the "Y" makes the final concentration of the solution at the nebulizer approximately 0.02 g rock per Kg solution.

Data were acquired using software supplied by the manufacturer. For both mass spectrometers, the counting time per mass was 10 s. Sample and wash solution uptake rates were similar to that of the MUN ICP-MS sinter package. With the set-up, the time spent per tube of solution was about 11 min.

The sequence of solutions for data acquisition was set up using calibration standards, calibration blanks (0.2 N HNO_3) and samples in a block size of 12 tubes. The calibration solutions were contained in 125 ml bottles. Two calibration solutions were prepared for this data acquisition protocol. These will be described below in Sec. 4.5 (External Calibration). In early runs, a third calibration solution was used to determine the sensitivity factors for 3 elements by surrogate calibration (Sn, W and Hg). Therefore, at the start, the sequence was STDA, STDB, STDC, flush, calibration blank, then a set of 8 samples which includes reagent blanks and reference materials all of which were analyzed as

unknowns. A flush tube (0.5 N HNO_3) was included to ensure a sufficient wash time after each set of standards was analyzed and to allow the intensity to fall before the blank solution was analyzed. Obviously, with STDC containing Sn, W and Hg (along with Sb, Lu and Pb), it was not desirable for any of these 3 elements to remain in the system and affect the count rates in the sample solutions. When the STDC was no longer used, the sequence for this package was shortened to STDA, STDB, calibration blank, followed by a set of 9 samples. The total time per cycle was about 2-¼ h. A full run of nine cycles took approximately 16-½ h.

4.4. Internal Standards

The internal standards chosen for this acquisition protocol were ^{45}Sc, ^{115}In and ^{187}Re. ^{238}U was added with the internal standards to monitor polyatomic ion formation. The ratio UO/U in the sample relative to the UO/U in the standards was used to normalize the interference correction. The selection of internal standards was based on the closeness of mass and on the premise that these internal standards have low natural abundance in the samples analyzed. Other important considerations in selecting internal standards include matching on the basis of first-stage ionization potential with the analytes, freedom from spectral interference, and neglible memory effects in the spectrometer system (Thompson and Houk, 1987; Gregoire, 1987; Beauchemin *et al.*, 1987; Beauchemin, 1989; Doherty, 1989).

Internal standardization involves the addition to the sample solution of a quantity of these elements that are not expected to be present in significant amounts in the original solution (Longerich *et al.*, 1990). Beauchemin (1989) observed that internal standards tend to be most effective for elements with *m/z* values close that of the internal standard and suggested the use of several elements throughout the target mass range, with the idea that the more elements used, the more accurate the mass-dependent correction is. However, that author cautions about the possibility of concomitant effects brought about by this step. She and co-workers (Beauchemin *et al.*, 1987) demonstrated either the signal enhancing or suppressing effect of Na, Mg, K, Ca, Cs, B, Al and U on the first row transition metals and attributed this to increased collision rate favoring greater ionization of the analytes (enhancement) or to oxide formation and deposition in the interface which may decrease the collision rate to a level where the recombination of ions with electrons is favored over the ionization of the atoms (suppression). Doherty (1989) used ^{99}Ru and ^{187}Re as the internal standards in the determination of 15 elements: ^{89}Y and the REEs (^{139}La to ^{175}Lu). He demonstrated the effectiveness of linear interpolation with mass as measured from Ru and Re, and subsequent application of drift and matrix correction to the 15 analytes. He validated this scheme for a variety of operating conditions and sample matrices.

Longerich *et al.* (1990) noted the need to have several internal standards spanning the entire mass range used as there is a mass dependent drift and matrix effect often observed in which light mass elements drift more than the heavy mass elements. This mass

discrimination affects matrix correction and as a result of this more correction is required for light than for heavy elements. The MUN ICP-MS sinter package currently determines 28 elements from Rb (mass 85) to U (mass 238) and the oxide of U (mass 254). In this package, Rb, Cs and Tl are used, with U as oxide monitor; Rb as the light elements' standard and Tl as the heavy elements' reference, and linear interpolation and extrapolation with mass is used for the other analyte masses (Longerich *et al.*, 1993a). This application in the sinter procedure, together with other calibration measures, has aided in producing excellent results for a variety of rock types represented by several geochemical reference materials studied (Longerich *et al.*, 1990). However, the concerns previously acknowledged when applying internal standardization over a wide mass range should always be recognized as these effects and others, such as matrix effects and drift, may not be easily identified by the analyst. As exercised in our Department, other laboratories would benefit by seeking a reasonable compromise between these concerns and the need to use a number of elements as internal standards to cover as wide a mass range as desired.

4.5. External Calibration

External calibration compares the intensity of an analyte signal in a standard solution that contains a known amount of that element to the intensity of the same element in the sample solution (Longerich *et al.*, 1990). For the data acquisition protocol under study, the sensitivities of the elements were determined from one of two calibration solutions.

Sensitivity is defined as the analyte signal (in counts per second, cps) in the standard solution divided by the concentration in the standard solution (ppb). These standard solutions were designated STDA and STDB and the concentrations used for analysis using the SCIEX ELAN 250 are shown in Table 4.1. Solutions used for the VG Plasmaquad are shown in Table 4.2, the difference in concentration from those in Table 4.1 was to take into consideration the greater sensitivity of the latter instrument. Calculation of element sensitivity accounted for the dilution by the pump which mixed in the solution containing the internal standards at the Y connector described earlier. Calcium and Ti in STDB were also used to calculate oxide interference factors on Co, Ni, Cu, Zn.

As described in Sec. 4.3 on Data Acquisition, a set of these calibration standard solutions was measured first in a cycle of the analytical sequence, followed by a flush, a calibration blank, then the sequence of 8 samples. The last cycle of a complete run (9 cycles) would end with another set of these standards, giving a total of 10 measurements on each standard solution. Calculation of the relative standard deviation for each of the elements in these standard solutions resulted in an estimate of instrumental drift for the entire run.

4.6. Surrogate Calibration

The sensitivities (cps/ppb solution) of 3 analytes (Sn, W, Hg) were determined by surrogate calibration. This was done because of potential memory effects for these

Table 4.1. Elements and approximate concentrations for STDA, STDB, STDC and spike for this study using the SCIEX ELAN 250 ICP-MS.

Element	STDA (ppb)	STDB (ppb)	STDC (ppb)	Spike (ppb)
Ca		40000		
Sc				700
Ti		200		
V	100			
Cr	200			
Mn	100			
Co	100			
Ni	200			
Cu	200			
Zn	200			
As	200			
Se	500			
Br		1500		
Mo	100			
Ag	50			
Cd	300			
In				100
Sn			200	
Sb	100		100	
Te	100			
I		100		
La	100			
Ce	100			
Pr	100			
Nd	100			
Er	100			
Tm	100			
Lu	100		100	
W			60	
Re				200
Hg			60	
Pb	100		100	
Bi	50			
Th	25			
U				100

Table 4.2. Elements and approximate concentrations for STDA, STDB, STDC and spike for this study using the VG Plasmaquad PQII+ ICP-MS.

Element	STDA (ppb)	STDB (ppb)	STDC (ppb)	Spike (ppb)
Ca		2000		
Sc				350
Ti		10		
V	5			
Cr	10			
Mn	5			
Co	5			
Ni	10			
Cu	10			
Zn	10			
As	10			
Se	25			
Br		75		
Mo	5			
Ag	3			
Cd	15			
In				50
Sn			20	
Sb	5		5	
Te	5			
I		5		
La	5			
Ce	5			
Pr	5			
Nd	5			
Er	5			
Tm	5			
Lu	5		5	
W			30	
Re				100
Hg			30	
Pb	5		5	
Bi	3			
Th	2			
U				50

elements as well as solution instability especially for Sn (Jackson *et al.*, 1990; Jenner *et al.*, 1990; Longerich *et al.*, 1990). Memory effects are signal enhancements in a sample resulting from erosion of elements deposited along the sample path during analysis of previous solutions. Jenner *et al.* (1990) described the use of the sensitivity of Zr to calculate that of Nb and Mo, and of Hf to calculate that of Ta and W, due to the potential for solution instability in the absence of significant HF in the solution. Jackson *et al.* (1990) reported on the use of Re as surrogate for the calculation of Os sensitivity in the analysis of PGEs. The waters/biological package at MUN uses Tl as surrogate for Hg (S. Jackson, pers. comm.). In this study, ^{121}Sb was used to calculate the sensitivity of ^{118}Sn, ^{175}Lu was used for ^{183}W, and ^{208}Pb for ^{201}Hg. Tin is said to be unstable in solution while Hg and W pose potential memory effects. Mercury and W are common laboratory contaminants. Mercury may be from glassware, and W usually is from sample preparation procedures especially those involving grinding with tungsten-carbide mills. Tungsten is also in reagents which presumably also involve grinding sometime in their preparation.

The sensitivities of Sn, W and Hg were calculated based on the relationships described in the MUN ICP-MS sinter package for calculating Nb sensitivity from the sensitivity of Zr, and for Ta from that of Hf (Longerich, 1996, pers. comm.). For example for Nb, this was done by multiplying the sensitivity of Zr by a sensitivity factor, F. In the MUN ICP-MS trace package, the sensitivity factors derived through surrogate calibration were: ^{93}Nb/^{90}Zr = 1.504; ^{95}Mo/^{90}Zr = 0.265; ^{181}Ta/^{177}Hf = 4.81; ^{182}W/^{177}Hf = 0.996. These values were calculated from 118 measurements in 59 runs on a solution containing these 6 elements.

The factors relating the sensitivity of the measured elements Sb, Lu and Pb to the sensitivity of Sn, W and Hg, respectively, include correction for molecular weight, isotopic abundance of the measured isotopes, mass discrimination and fractional ionization (Longerich, 1997, pers. comm.). The calculation for Sn sensitivity was done, as follows:

$$S_{Sn} = S_{Sb} * \textit{Sensitivity Factor}$$

where, S_{Sn} = sensitivity of tin

S_{Sb} = sensitivity of antimony

Sensitivity Factor = composite factor that is the product of 4 components due to differences in molecular weight, isotopic abundance, mass discrimination and fractional ionization.

The components of the *Sensitivity Factor* that are known are those for molecular weight and isotopic abundance (Longerich, 1997, pers. comm.). Those due to mass discrimination and fractional ionization are dependent on the mass spectrometer used, and ion lens set-up and plasma conditions. Mass discrimination is the change in molar sensitivity with mass. The factor varies with ion lens setting but is expected to be small for small mass differences, i.e., the factor will be close to one. Fractional ionization, which includes monoisotopic ion and oxide formation, is a factor since, while many elements are close to

100% ionized, elements with high ionization potentials are much less than 100% ionized. Of the 3 elements calculated by surrogate calibration, Hg has a high ionization potential of 1007 kJ mol^{-1}, and is expected to be less than 100% ionized. A higher fractional ionization gives a higher sensitivity. This factor is a function of plasma optimization and is close to one for elements with low ionization potential and low oxide formation, etc..

In the calculation of the sensitivity factor for the pair Sn-Sb, therefore, the following equation was used:

$$Sensitivity\ Factor = (Abund_{Sn}/Abund_{Sb}) * (M.W._{Sb}/M.W._{Sn}) * (F'_{Sn/Sb})$$

where: $Abund_{Sn}$ = natural abundance of tin

$Abund_{Sb}$ = natural abundance of antimony

$M.W._{Sb}$ = molecular weight of antimony

$M.W._{Sn}$ = molecular weight of tin

$F'_{Sn/Sb}$ = partial sensitivity factor for Sn-Sb to account for small differences due to mass discrimination and fractional ionization.

The partial sensitivity factor, F', was determined experimentally using the third standard solution, STDC, in the ICP-MS environmental-exploration runs. This standard solution contained Sn, Sb, Lu, W, Hg and Pb. The calculation shown above for Sn-Sb was similarly attempted for the pairs W-Lu and Hg-Pb, substituting W or Hg for Sn and Lu or

Pb for Sb in the equation given. From these 3 pairs, only the pair Sn-Sb proved successful in recovering published element values for the standard reference materials utilized (PACS-1 and MESS-2). PACS-1 represented the high concentration end for expected samples while MESS-2 was for the low-grade metal level. Their relationship was also examined in terms of responses from the geochemical reference materials MRG-1, BHVO-1, AGV-1, G-2, BCR-2.

In the first 5 runs using the ICP-MS environmental-exploration (env-exp) package, calculation for the partial sensitivity factor, F', gave values of 1.62, 1.62, 2.0, 2.2, 2.2 for Sn-Sb. The results for the pair W-Lu were not as definite as that of Sn-Sb although reasonable on a per run basis. For W-Lu, the estimates of F' in the first 5 ICP-MS environmental-exploration runs were 0.45, 0.95, 1.0, 1.4, 0.75. The high variability may be due to laboratory contamination from W in the reagents. The results for Hg-Pb were not satisfactory and this was due, not to the calibration itself but most probably, to volatilization loss of Hg during sample digestion. The evaporation of the sample solution to incipient dryness during preparation, although at a moderate temperature of 70 °C, must have been enough to volatilize Hg. McLaren *et al.* (1988) in their ICP-MS analysis of PACS-1 avoided the loss of Hg by not completely boiling off the HNO_3, even if the temperature used at this step was 170 °C. A separate sample digest may be necessary for the analysis of Hg in rocks, sediments or soils in this laboratory which should be part of future research as the element is important in many geological and environmental work.

4.7. Data Reduction

Each step used in the data reduction procedure described herein is also presented in a more algorithmic manner in Appendix B, that is without discussion.

Background was calculated from the mean of all the acid (calibration) blanks in the run. These calibration blanks were solutions of 0.2 N HNO_3, the same acid used for STDA and STDB. The use of the mean reduces the detection limit since the uncertainty of the blank correction is made smaller by using multiple blanks. The median would have been more resistant to the presence of outliers such as when some calibration blanks give unusually high background due perhaps to some error in measurement or a fluctuation in operating condition. However, by the same token, using the mean alerts the analyst to review the run which could indicate the reason (e.g., sipper malfunction) for the high blanks and the portion of the batch that may have to be junked. Other conventions may be used for the background, i.e., in lieu of the mean, the maximum or the minimum in a particular run may be used. Use of the maximum would be an attempt to account for the highest possible background value that the run was characteristic of. However, it may unduly increase the background in cases where the maximum was exceptionally high and was only due to a single tube that was contaminated, and thus will bias against samples with low background.

In the present ICP-MS analysis, several latter runs had very high backgrounds for the transition elements, especially Ni and Cu. In one run (run name: Nov28117), the Ni counts in the calibration blanks were significantly higher than the counts in the sample solutions, resulting in negative values for Ni in the ppm calculation for almost all samples. This could have been an indication of memory effects for this element, or signal enhancements due to deposition and subsequent erosion of analyte ions. Nickel could have stayed in the system after the analysis of previous samples using the PGE scheme described by Jackson *et al.* (1990), or from the nickel material itself used for the sampler and skimmer in the ICP-MS that have begun to degrade, or from laboratory contamination.

The background value (mean of all calibration blanks) was subtracted from all gross intensities. For the internal standards, Sc, In and Re, zero was used. While the background is actually slightly higher, due to the fact that all gross count rates were high, there will be insignificant difference if zero was used or the actual rate, which was probably less than 10 cps, was used.

The interference factors due to polyatomic ion formation were calculated from STDB. The 4 interferences are: $^{43}Ca^{16}O$ which interferes with the determination of Co at mass 59; $^{44}Ca^{16}O$ which interferes with the determination of Ni at mass 60; $^{49}Ti^{16}O$ which interferes with the determination of Cu at mass 65; and $^{50}Ti^{16}O$ which interferes with the determination of Zn at mass 66. The interference factors are ^{59}(CaO)/Ca, ^{60}(CaO)/Ca, ^{65}(TiO)/Ti, and ^{66}(TiO)/Ti. This is further discussed in Sec. 4.8 (Oxide Interferences).

These interference factors were corrected using the UO/U of the sample. It is assumed that if either of these ratios is changed all the interference factors will change in the same proportionality (Lichte *et al.*, 1987). This is only a first approximation, but over the small range used, it should be a very reasonable approximation. The contribution by the interferents was then calculated and subtracted from the blank corrected intensities of the appropriate masses.

The sensitivity of the instrument for each element was calculated by dividing each element count rate (using the blank corrected intensities) by the actual, known concentration of that element as used in the standard solutions. The matrix correction factors were calculated from the internal standards used. The assumption is that the intensity of the internal standard is affected in the same way as the intensity of the analytes. A more realistic estimation should also consider the elements' ionization potential, however, the entailing derivation of that complex relationship was not attempted here. A linear interpolation, or extrapolation, of the matrix correction factors was made for intermediate masses. Drift and matrix are chemometrically multiplicative and can not be easily separated (Longerich, pers. comm.), so both are corrected by internal standardization.

The (not matrix-corrected) concentration of each unknown sample solution was calculated from the blank- and interference-corrected count rate and the sensitivities drift-corrected to the first calibration solution in the block. Matrix-correction was then applied to the solution concentration. With the sample solution concentration calculated from the actual

weight of rock dissolved during digestion, and after considering the several steps of dilution used, the concentration in the solid was then determined.

4.8. Oxide Interferences

As stated in Sections 4.2 and 4.7, oxide interferences on the transition metals Co, Ni, Cu and Zn were expected from species formed by Ca and Ti as the target sediment samples would normally contain minerals such as calcite and rutile. In the data reduction sequence described above, calculation of interference factors and the interference correction of the background-corrected count rates were done after background correction and before application of matrix correction. This section describes in more detail some aspects involved in the correction for oxide interference.

As previously mentioned, the oxide interference correction factors were calculated from STDB which contained Ca and Ti. The signals at ^{59}Co, ^{60}Ni, ^{65}Cu and ^{66}Zn were measured in this standard solution. The percent oxides were obtained by dividing the blank-corrected mean intensities at mass 59, 60, 65 and 66 by the appropriate blank-corrected mean intensity of the interferent mass. These factors were then normalized to STDA by multiplying each with the mean UO/U ratio in STDB divided by the mean UO/U ratio in STDA. The calculated interference factors from the 9 runs are tabulated in Table 4.3 and shown in Fig. 4.1. Table 4.3 also shows the mean and median oxide contribution from these runs.

Table 4.3. Mean interference factors in the 9 ICP-MS env-exp runs.

Run	^{43}CaO/ Ca	^{44}CaO/ Ca	^{49}TiO/ Ti	^{50}TiO/ Ti	UO/U std A
1 - jun05117	0.37%	0.68%	0.96%	0.36%	5.89%
2 - jun25117	0.17%	0.46%	1.10%	0.59%	5.93%
3 - jun27107	0.28%	0.72%	1.25%	0.79%	6.32%
4 - jul02147	0.28%	0.70%	1.94%	0.88%	6.33%
5 - jul03107	0.42%	0.86%	1.77%	0.85%	7.92%
6 - jul14117	0.40%	0.90%	1.43%	0.65%	7.87%
7 - nov28117	0.06%	0.07%	3.13%	0.00%	2.43%
8 - jan27108	0.18%	0.00%	0.00%	3.23%	1.77%
9 - jan29108	0.31%	0.00%	0.00%	0.00%	2.43%
$mean_{all}$=	0.28%	0.63%	1.65%	0.59%	6.10%
$median_{all}$=	0.28%	0.70%	1.43%	0.65%	6.32%
std. $dev._{all}$=	0.13%	0.28%	0.74%	0.32%	1.83%
$mean_{1-6}$=	0.32%	0.72%	1.41%	0.69%	6.71%
$median_{1-6}$=	0.33%	0.71%	1.34%	0.72%	6.33%
std.$dev._{1-6}$=	0.09%	0.16%	0.38%	0.20%	0.94%
$mean_{7-9}$=	0.18%	0.02%	1.04%	1.08%	2.21%
$median_{7-9}$=	0.18%	0.00%	0.00%	0.00%	2.43%
std.$dev._{7-9}$=	0.13%	0.04%	1.81%	1.86%	0.38%

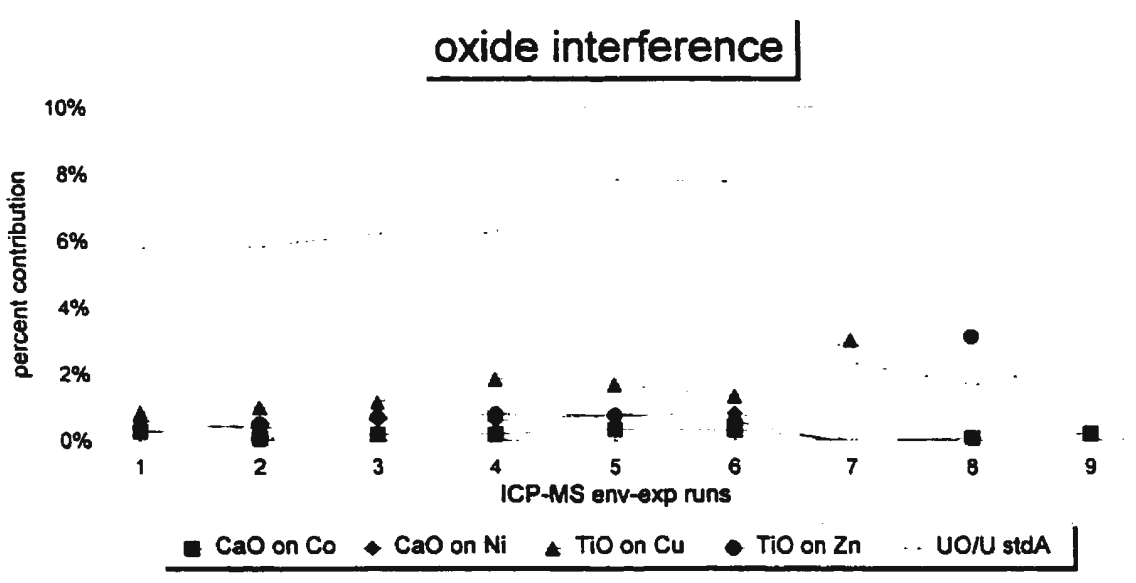

Fig. 4.1. Average ratios of $^{43}Ca^{16}O/Ca$, $^{44}Ca^{16}O/Ca$, $^{49}Ti^{16}O/Ti$ and $^{50}Ti^{16}O/Ti$ (filled symbols) from 6 ICP-MS env-exp runs in the SCIEX (runs 1-6) and 3 runs in the VG (runs 7-9). The average UO/U ratio for each run (open symbol) calculated from STDA is also indicated.

The first 6 runs were done in the SCIEX ELAN ICP-MS while the last 3 analyses were performed in the VG PlasmaQuad. The corresponding averages of the UO/U ratio normalized to that in STDA for each run are also indicated. Figure 4.1 plots the percent contribution from the oxides on the respective analyte masses, including the UO/U ratio in each run. The x-axis of this graph corresponds to the ICP-MS environmental-exploration package run number. The transfer from the SCIEX to the VG clearly corresponded to a decrease in oxide formation as shown by the ratio UO/U. The first 6 runs in the SCIEX unit averaged 6.7% and ranged from 5.9% to 7.9%. The last 3 runs which were in the VG averaged 2.2% and fluctuated between 1.8% and 2.4%. Routine tuning for oxide ion formation in the SCIEX ELAN at MUN sets the ratio UO/U to about 6%, or a ThO/Th ratio of about 10%, preferably slightly lower. Further lowering of UO/U results in lower sensitivity which is already approximately 50% of the maximum sensitivity. Runs 5 and 6 of the environmental-exploration package gave oxide ratios slightly higher than this limit although the overall sensitivity of the analytes was not significantly affected. However, the analyses were done when the SCIEX was developing mechanical and electrical problems in its electronic circuitry or elsewhere, and the opportunity for re-analysis was becoming unlikely. It would have been ideal to be able to reproduce results obtained from the SCIEX as oxide formation in this unit appeared to be more "stable" although higher. This was indicated by the contribution from Ca and Ti oxide species on the respective analyte signal with averages of 0.32% for CaO on Co, 0.72% for CaO on Ni, 1.41% for TiO on Cu, and 0.69% for TiO on Zn. These values are not as severe as that normally recorded for the rare-earth elements (Jenner *et al.*, 1990) but nonetheless constitute significant

enhancements especially for samples with low concentrations of these particular metals occurring together with an high abundance of the major elements Ca and Ti.

In the VG system, the augmentation on analyte signal from oxide formation featured some unusually high values for each of these 4 analytes although not in the same run. The highest of these values would have been from a run that was rejected due to very erratic UO/U trend through the several samples analyzed eroding the validity of the results for this particular batch of samples. This run stopped after just one cycle (run name: Jan26108). The average $^{44}Ca^{16}O/Ca$ in this run was 15.91%. Without this run, the Nov28117 run had the highest interference factor for $^{49}Ti^{16}O$ on ^{65}Cu (3.13%); while the Jan27108 run contained that for $^{50}Ti^{16}O$ on ^{66}Zn (3.23%). All of these runs were done using the VG system.

In Table 4.3, it is indicated that 2 of the runs in the VG show 0% contribution from oxide formation on the signal of Ni and Zn and 3 runs show none on Cu. This resulted from particularly high count rates in the acid blanks for these elements which produced negative correction factors. Only the factors for Co had not produced a negative factor and has consistently yielded an enhancement from a CaO species. In the study by McLaren *et al.* (1987) on solutions of the sediment reference material BCSS-1 no intereference was cited for Co and Ni at *m/z* 59 and 60, respectively, although their Fig. 2 spectra hinted at the presence of an enhancement, albeit minor, at mass 59 from the BCSS-1 solution. The degree of this signal increase can be critical if not taken into consideration especially in the

analysis of sediments which most likely contain carbonates as matrix material.

To examine how the metal-oxide over metal ratio (MO/M) behaved during a run and how it was related to UO/U in that same run, the ratios from $^{43}Ca^{16}O/Ca$ (interferent on ^{59}Co), $^{44}Ca^{16}O/Ca$ (on ^{60}Ni), $^{49}Ti^{16}O/Ti$ (on ^{65}Cu) and $^{50}Ti^{16}O/Ti$ (on ^{66}Zn) calculated from each measurement of STDB were plotted together with the corresponding UO/U. Figure 4.2 shows a typical run done in the SCIEX (Jun05117) and illustrates an increase in UO/U from the first STDB tube (Tube number 2) to the last STDB tube in the run with the average for the whole run at around 6%. This increase coincided with a general decrease in MO/M ratios, except for $^{43}Ca^{16}O/Ca$, but the general behavior was well characterized at less than 2% MO/M. In contrast, a run in the VG (Nov28117) showed some fluctuations in MO/M during the run (Fig. 4.3). Although, the ratio UO/U was constant at slightly above 2%, $^{49}Ti^{16}O/Ti$ and $^{50}Ti^{16}O/Ti$ showed some "noise". The more "level" trend of $^{43}CaO/Ca$ and $^{44}CaO/Ca$ in the graph is more deceiving because several of the tubes were assigned a value of zero percent after blank correction produced negative factors. Nevertheless, the higher values obtained for the TiO species seem to confirm the relationship of the MO/M ratio to the strength of the metal-oxygen bond as described by McLaren *et al.* (1987).

The interferences on Cu and Zn from TiO species were the more problematic in the analysis of BCSS-1 (McLaren *et al.*, 1987). They therefore placed special attention in modifying operating conditions to strike a reasonable compromise between oxide

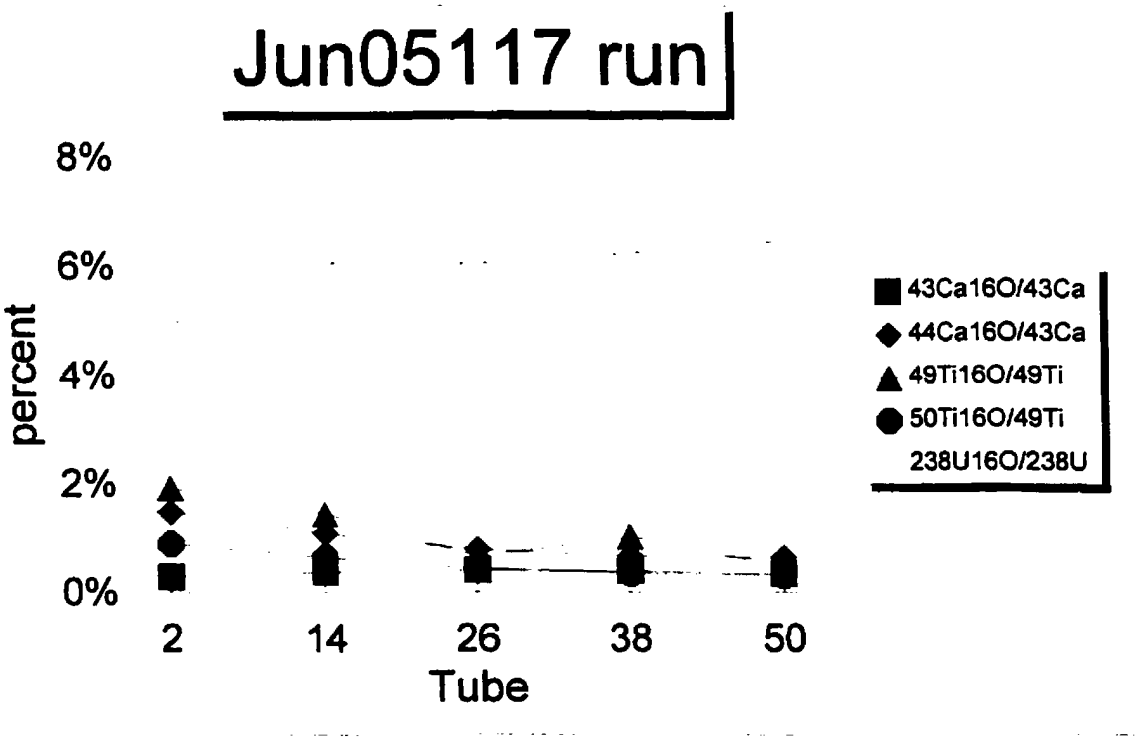

Fig.4.2. Plot of MO/M ratios on mass 59, 60, 65 and 66 with corresponding UO/U measured from STDB tubes in run Jun05117, indicating a more stable oxide formation.

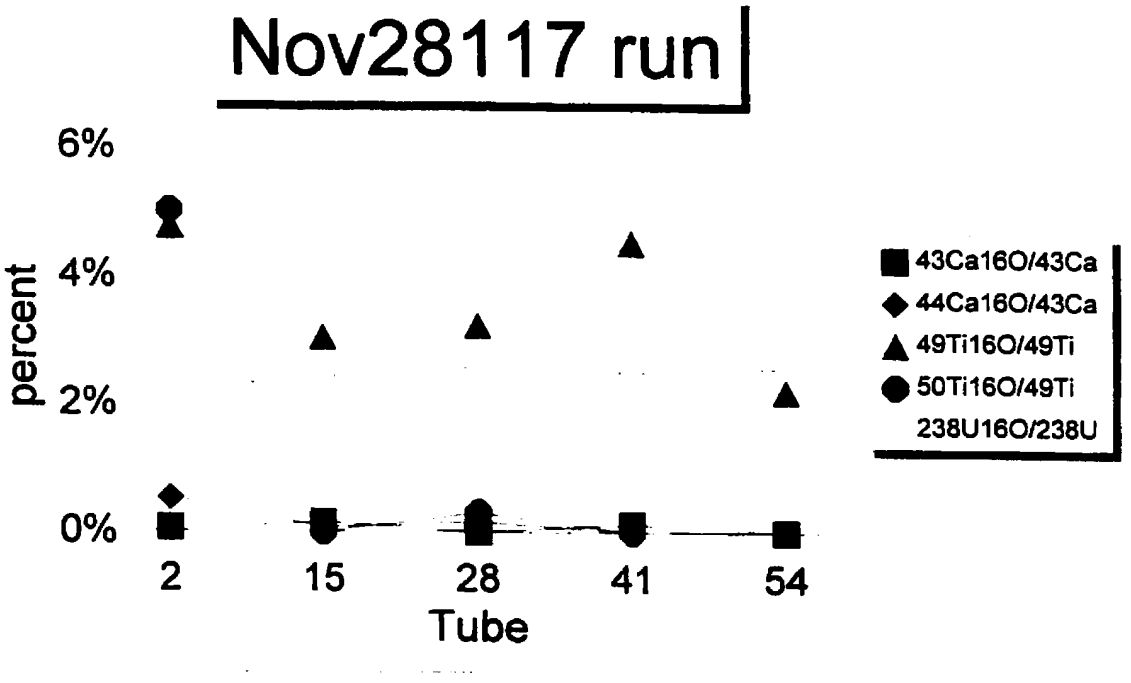

Fig.4.3. Plot of MO/M ratios on mass 59, 60, 65 and 66 with corresponding UO/U measured from STDB tubes in run Nov28117, indicating more "noise" in the TiO species.

formation and sensitivity. Significant interference on ^{65}Cu and ^{66}Zn were still indicated and it was suggested that ^{68}Zn be used instead as it appears to have no overlap from TiO. The dependence of oxide and/or hydroxide formation, as well as the relative proportion of singly and doubly charged ions of an element, on plasma operating conditions has been emphasized in the works of Vaughan and Horlick (1986) and Longerich *et al.* (1986). It is therefore imperative to continuously look into these functions as they affect the sensitivity of analytes especially in relation to the generation of other potential interferent species from the very varied matrices that geological samples possess.

4.9. Sensitivity and Detection Limits

Sensitivity of most of the analytes was measured from the standard solutions, STDA and STDB. This was obtained specifically by the equation:

$$Sensitivity = count\ rate / ppb$$

with *count rate* = the blank corrected count rate for the analyte

ppb = the actual concentration of the element in the standard solution (for the solution delivered to the nebulizer).

Figure 4.4 is a plot of the element count rate per ppb normalized to the natural isotopic abundance as measured from the standard solutions of the 9 ICP-MS environmental-

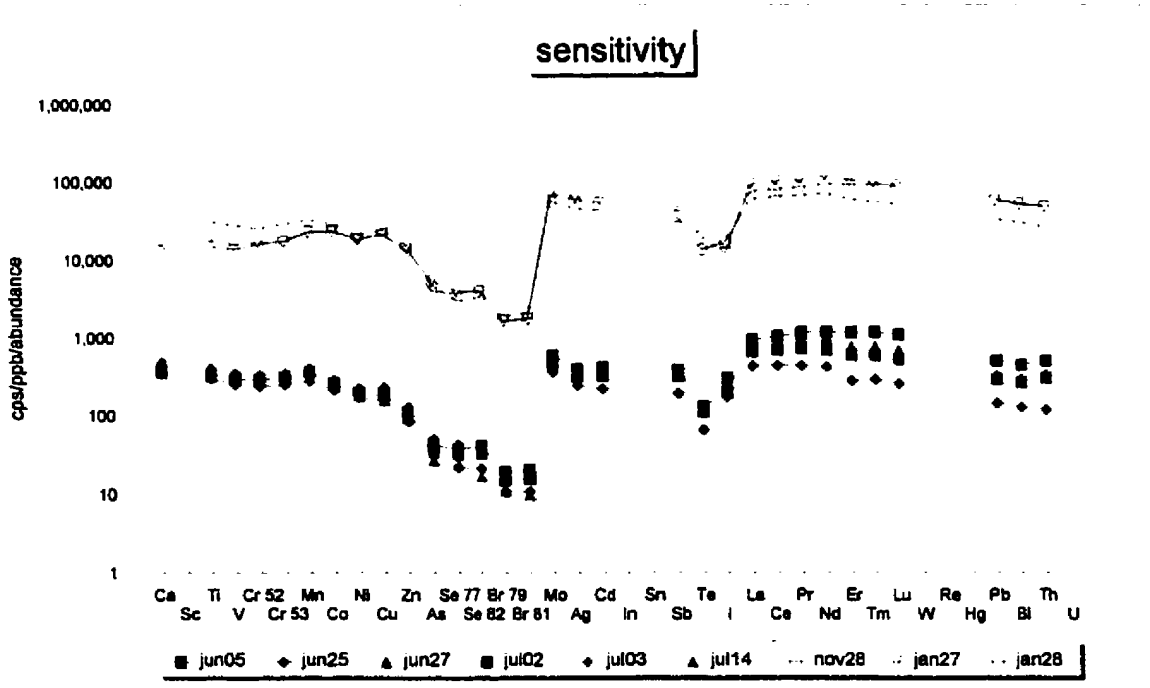

Fig. 4.4. Plot of the element count rate per ppb normalized to isotopic abundance as measured from standard solutions STDA and STDB from 6 ICP-MS env-exp runs using the SCIEX (filled symbols) and 3 runs using the VG (open symbols).

exploration runs. No values are plotted for the internal standards Sc, In and Re and the oxide monitor U, as well as for the elements calculated for surrogate calibration, Sn, W and Hg. The figure clearly portrays the difference in the sensitivity of the instruments used. The first 6 runs were done with the SCIEX; while the last 3 runs were with the VG. The results from the latter instrument, which is of greater sensitivity, reflected values that were approximately 2 orders of magnitude higher than those from the SCIEX.

As in the sensitivity calculation, the detection limits of the analyte solutions as derived in each run were calculated from the standard solutions using the equation:

$$limit\ of\ detection = 3\ \sigma_{Bkg}\ /\ Sensitivity$$

with $3\ \sigma_{Bkg}$ = 3 x standard deviation of the analyte signal in the calibration blank, in cps

Sensitivity, as calculated above. Note that no matrix correction is used as it is not a significant factor.

Jenner *et al.* (1990) cited excellent detection limits especially for the monoisotopic rare-earth elements but stressed that the values are not fixed and are compromises between sensitivity and lower oxide interferences. They added that the reported detection limits are only for routine instrument configuration and do not represent the best of which the technique is capable. In the present environmental-exploration package, the detection limits for the several REEs included in the suite compare well with previous works in the

Department. Toward the lighter elements, however, the detection limits are generally higher, especially for the transition metals Ni, Cr, Cu and Zn. Lead displays a high detection limit as well. The analysis of these metals is much more prone to contamination. Lead may be affected by reagent impurities from particulate air or by laboratory contamination while Ni may be from nickel-bearing labwares. Routine use of clean bench techniques and, as previously noted, double distillation of acids and use of nanopure (deionized, distilled) water are undertaken to minimize these unwanted contributions to analyte concentration. Other practices, such as cleaning (acid-washing) of sample and reagent vessels and containers, are also mandatory. Review of protocols should be regular with the aim of upgrading the level of cleanness in the laboratory to further reduce the risk of contamination. As discussed below in Sec. 4.10 (on Method Blanks), contamination from these common laboratory elements easily poses an area of concern in low-level trace metal determinations.

Some elements, particularly Ni, suffer from horrible memory effects as mentioned above. These effects, which are signal enhancements in a sample resulting from erosion of elements deposited along the sample path during a previous analysis, could take place anywhere in the sample path, e.g., the nebulizer, spray chamber, torch, sampler cone or skimmer cone. A previous analysis of samples for precious metals utilizing the method described by Jackson *et al.* (1990) may have left transition metals in the ICP-MS system.

The detection limits for the 9 runs performed using the environmental-exploration package reveals that the last 3 runs generally show higher values compared with the first 6 runs (Fig. 4.5). Again, these last 3 runs were those done in the VG. The elements Cr, Mn, Cu, Zn, As, Cd, Sn and Pb showed that VG detection limits were always higher than those from the SCIEX. Generally higher results from the VG but with some overlap with detection limits from the SCIEX were those for the elements V, Co, Ni, Mo and Bi. One would expect to have better detection limits from the more sensitive instrument, the VG, compared to the SCIEX but this does not seem to be the case here for these elements, most of which are transition metals. This was most probably due to the very high or erratic background concentrations for these elements, especially for Cu and Ni. It is possible that if more concentrated solutions are used in the VG (*e.g.*, using the SCIEX dilution factor) the signals would be high enough to rise above the background fluctuation. However, it is also possible that the higher concentration would have switched the VG detector mode from digital to analogue counting, which unfortunately was not functioning at the time. As discussed earlier, the calibration blanks gave high levels, even up to thousands of counts on these masses. These metals are prone to contamination from a variety of sources, such as the acids or reagents used, improper cleaning or handling of laboratory wares, or degradation of the atmosphere in the laboratory. This could be amended by more careful practices in the sample handling and digestion protocols and acid distillation, improved procedures in cleaning sample and reagent bottles and tubes, HEPA-filtration of instrument room atmosphere and frequent testing of reagents and blanks.

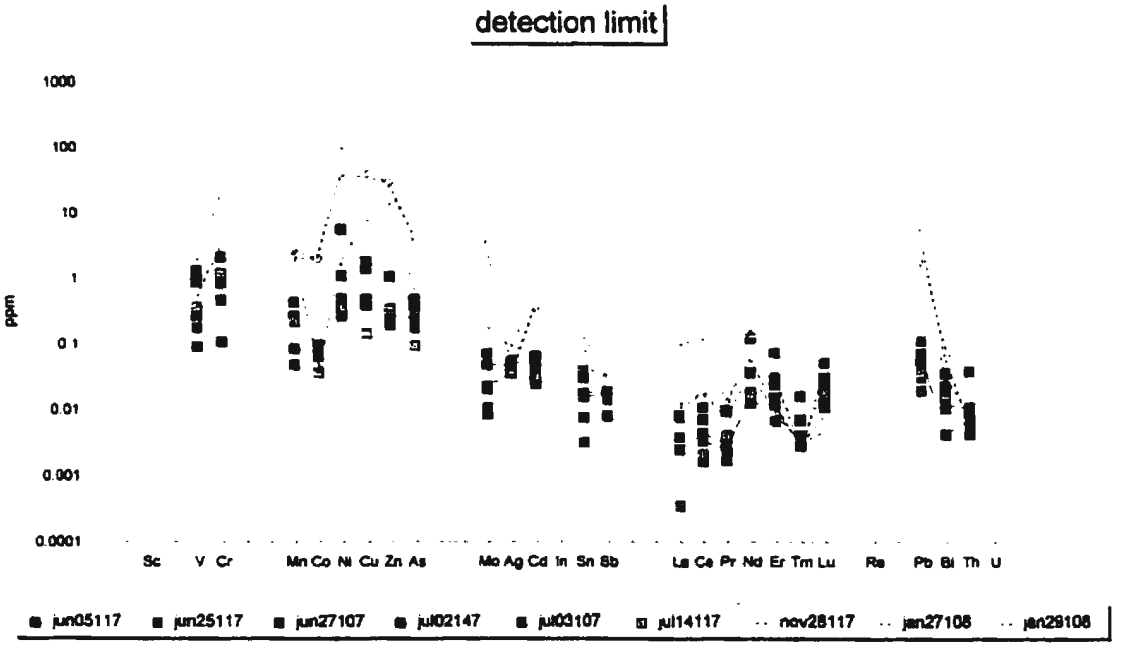

Fig. 4.5. Plot of detection limits for 23 elements measured using the ICP-MS env-exp package in 6 runs done in the SCIEX (filled squares) and 3 runs done in the VG (open diamonds). Dilution in the SCIEX was approximately 0.5 g rock/Kg solution while dilution in the VG was approximately 0.02 g rock/Kg solution.

Similar detection limits was shown by the 2 mass spectrometers for Ag, Sb, Pr, Tm and Th. The rare earth elements (La, Ce, Pr, Nd, Er, Tm and Lu) gave detection limits that were generally similar, as the blanks were generally low, less "noisy" and more stable. The results also suggest that depending on the purpose of a study there may still be room for compromise in using instrument parameters that allow lower sensitivity for the lighter elements in this package although perhaps greater isobaric overlap from oxide species.

4.10. Method Blanks

Method, or procedural, blanks were included in each batch of samples and reference materials digested through the high pressure vessels. These method blanks, numbering a total of 13, carried the reagents used through the dissolution, work-up and analysis in a similar manner as the actual samples. The quality of results from these method blanks will give an indication of the overall data quality, particularly how well the values obtained for the samples reflect the actual element concentration in those samples.

The results for most of the method blanks were generally at or near the detection limits for most elements, especially V, Mn, Cu, As, Mo, Ag, Cd, Sb, La, Ce, Pr, Nd, Er, Tm, Lu, Bi and Th in the 9 ICP-MS environmental-exploration runs. In 5 of these runs, the values of some of the transition metals (Cr, Co, Ni, Zn) and Sn and Pb were higher than the respective limits of detection by several factors. In the Jan27108 run, Cr in one method blank was higher than the detection limit (D.L.) by a factor of 5. Cobalt in two method

blanks was higher than the D.L. by a factor of 4 to 5 in Jun05117 and Jul14117; Ni by a factor of 7 to 10 in Jun27107, Jul03107 and Jul14117; Zn by a factor of 5 to 100 in Jun05117, Jun27107, Jul03107 and Jul14117; Sn by a factor of 5 to 7 in Jun05117 and Jul03107; and Pb by a factor of 4 in Jul03107. These values may indicate contamination especially for Ni and Zn. Three different method blanks (labeled 8-B, B-516 and B-707) gave high values for Ni; while only one blank (8-B) was involved for Zn. 8-B was traced to be the blank into which a small dark-colored flake fell during addition of HF-boric solution. Another method blank (7-B) that was prepared at the same time as 8-B gave acceptable (at or near D.L.) results. Both blanks were analyzed in 2 runs (Jun27107 and Jul02147) and gave similar Ni and Zn values in these runs. It is therefore highly likely that the foreign matter that was accidentally dropped into the polypropylene container for 8-B caused the higher values for Ni (factor of 10) and Zn (factor of 100) in this particular blank.

The behavior of these trace metals may indeed result from contamination during every stage of the sample preparation and analysis. The elevated values for Cr, Co, Ni, Zn, Sn and Pb in some (but not all) of the method blanks indicate that sample digestion or solution tube handling preparatory to analysis may easily compromise the results of the whole run. Fortunately, for this study, the element concentrations in the samples were significantly higher, generally by 2 orders of magnitude, than the concentrations obtained in the blanks themselves. However, as stated in the previous section (Sec. 4.9), observance of clean and careful procedures throughout the analytical process assures data quality

besides attaining minimum or even no wastage in the time, effort and materials put into the laboratory.

4.11. Results and Discussion

The environmental-exploration (env-exp) package was used to analyze several geochemical reference materials. These GRMs were prepared using the procedure described in Section 3.3.3. The results for V, Cr, Co, Ni, Cu, Zn, As, Mo, Ag, Cd, Sn, Sb and Pb were compared with compiled values (Govindaraju, 1989) using the following XY plots and are discussed below. From the original 29 masses selected at the start of the study, 6 elements (Se, Br, Te, I, W and Hg) have not given good results, likely due to loss through volatilization during sample dissolution or to reagent contamination. Calculation of the sensitivity of W and Hg using surrogate calibration, as discussed earlier (Sec. 4.6), proved unsuccessful not because of error in calibration but most likely due to loss of the element from the sample during evaporation to dryness.

There was excellent agreement with literature values for the elements V, Co, Cr, Ni, Sn and Sb, except when values approach detection limits (Figs. 4.6). It seems that even with higher detection limits for Cr and Ni as described in a previous section (4.9), the samples chosen for this comparison contain concentrations of these metals that are much higher than the detection limits. Zinc and Pb indicated reasonable agreement although there occurs some spread in the data. This was shown for Zn notably by PACS-1 as one analysis

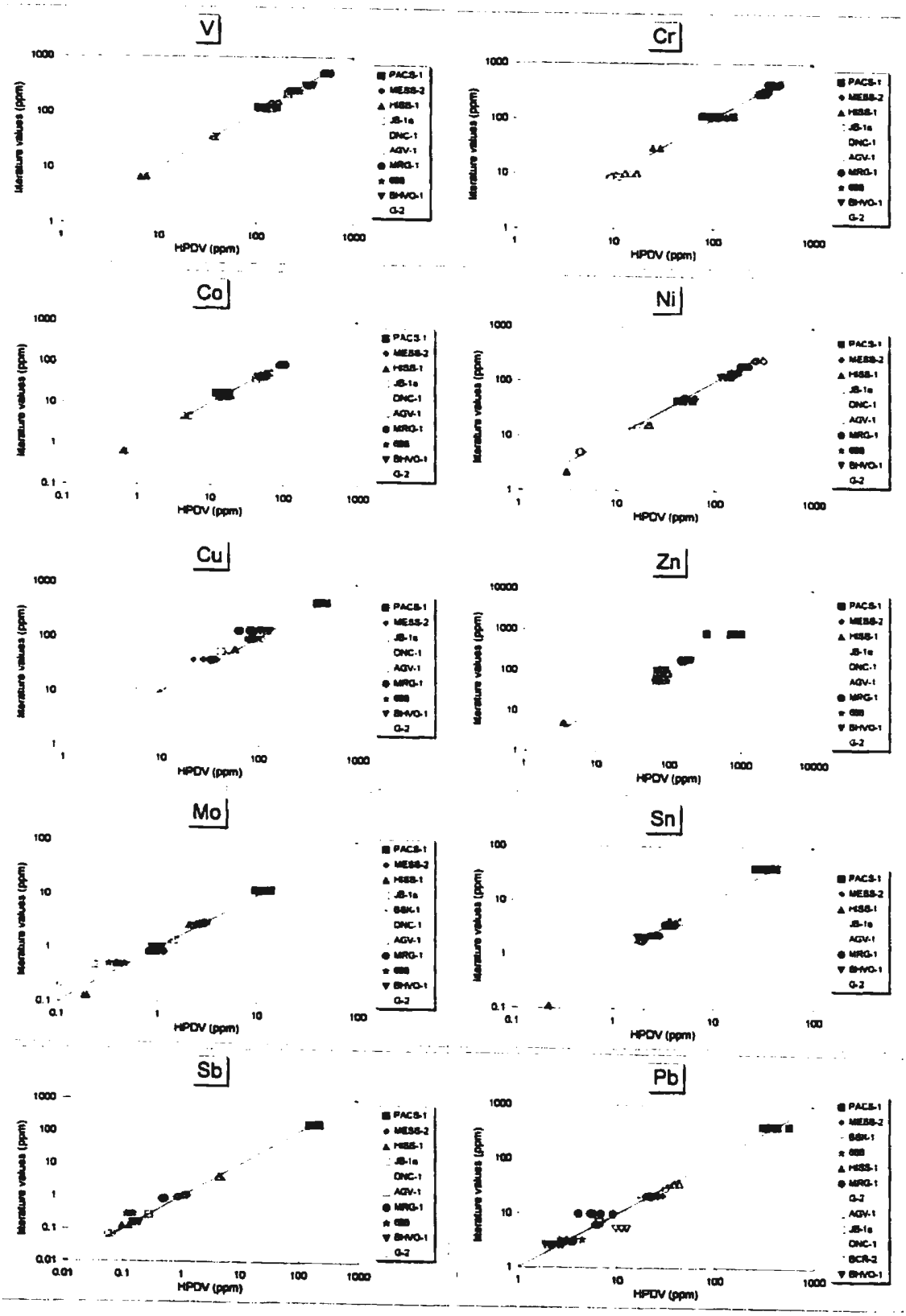

Fig. 4.6. Plot of V, Cr, Co, Ni, Cu, Zn, Mo, Sn, Sb and Pb values of several geochemical reference materials: literature values vs. those obtained using the ICP-MS env-exp package following digestion with the high pressure digestion vessels (HPDV).

of this sediment GRM gave lower values from the experimental package, and for Pb by PACS-1, MRG-1 and NBS-688. There was significant agreement in the results for Cu and Mo although there was a slight tendency for higher literature values for most of the GRMs. The sediment reference materials displayed excellent conformity for Mo but there was some underestimation of Cu in MESS-2 by the ICP-MS package. Cadmium gave good results for PACS-1 and partly for DNC-1 and G-2 but the bulk of the reference materials gave higher values in the package under study (Fig. 4.7). It is not certain whether the environmental package is able to consistently give higher results for this element, which would imply the possibility of attaining better accuracy, because the concentration levels shown were approaching the element's limit of detection (mean = 0.045 ppm). For 2 elements, As and Ag (Fig. 4.7), results for most of the GRMs were near detection limits. An excellent agreement was, however, shown for As in MESS-2 which would support precise detection of the element in the XRF trace package. The MUN XRF trace package averaged approximately 21 ppm As in 5 analyses of the GRM in 1996 and 1997. NRCC (1995) gave a certified value of 20.7 ppm As in MESS-2. Excellent correspondence was also shown for PACS-1 between the ICP-MS environmental-exploration package and the literature value. This correspondence, however, can not be similarly compared with the MUN XRF results as this reference material is used as calibration standard for the element in MUN XRF trace runs. Results for Ag for the 7 reference materials analyzed all showed higher values in the environmental package although again they hover about the limits of detection for the first six runs from which these values were obtained (mean = 0.046 ppm).

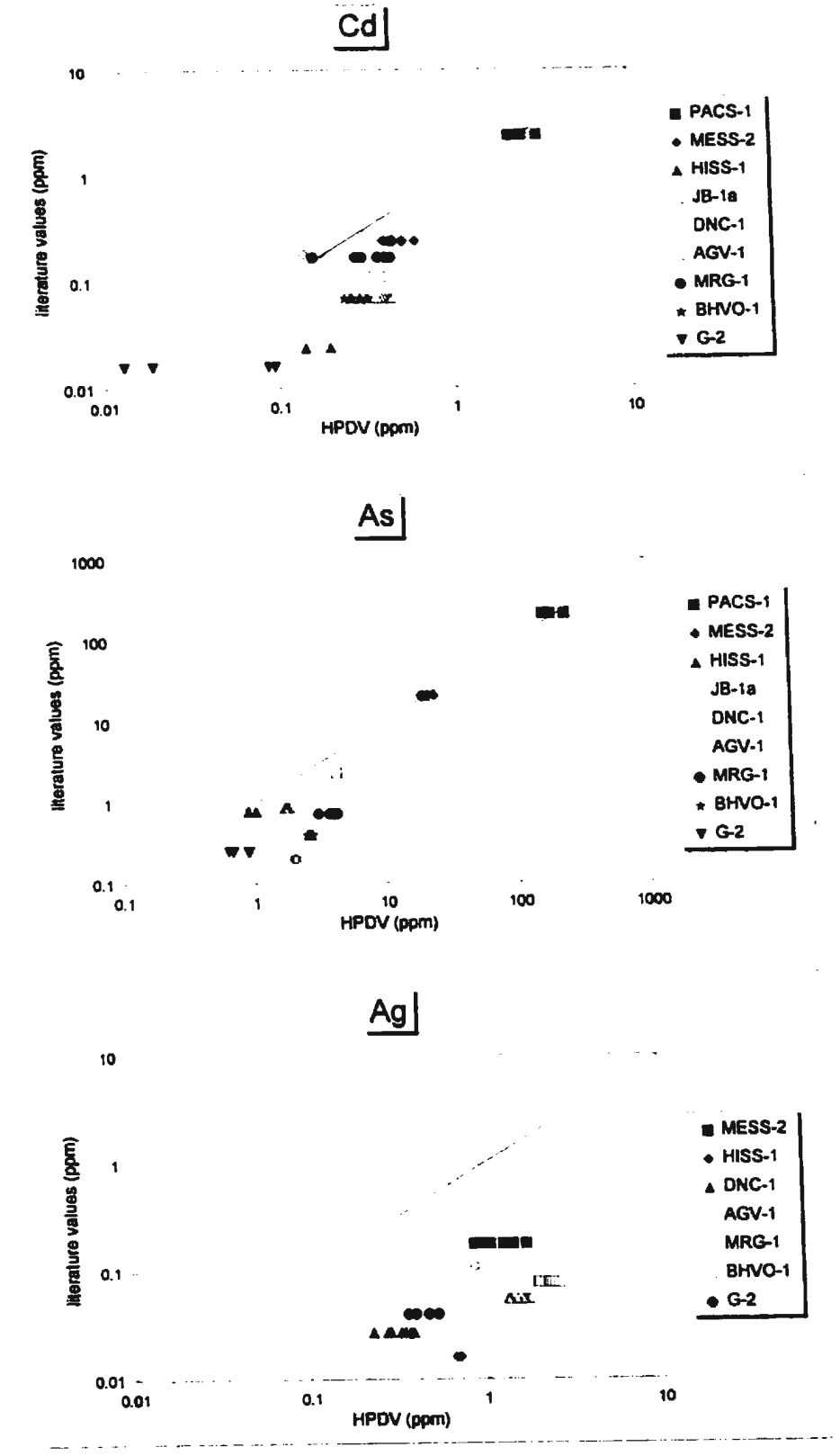

Fig. 4.7. Plot of Cd, As and Ag values of several geochemical reference materials: literature values vs. those obtained using the ICP-MS env-exp package following digestion with the high pressure digestion vessels (HPDV).

In these first runs of the ICP-MS environmental-exploration package, a sample being characterized as an in-house reference material was also included. Replicates of this sample were labelled m10356q and m10357w. In Figure 4.8 are plots comparing the results for this material using the MUN XRF trace package and the MUN ICP-MS trace package with those from the environmental-exploration package. It is clear from Fig. 4.8 that there is very good conformity between the results for 11 elements common to the ICP-MS trace and environmental packages (Mo, La, Ce, Pr, Nd, Er, Tm, Lu, Pb, Bi and Th) as indicated by the tight cluster of data points. Compared with the XRF results, the new package showed good correspondence except for Ni. The package was also slightly off for Ce and As. Nickel showed remarkably low values in the XRF, and this could be a result of calibration in the XRF which utilizes the reference material DTS-1 (Ni concentration of 2,360 ppm) as its calibration standard for the element, or to inherent Ni background problems in the XRF (Longerich, 1995), probably from Ni in the instrument. The analysis of Ni is also said to be problematic because of potential sources of contamination in solution work as mentioned earlier. For most of the elements, however, the results provide very good correspondence and constitute additional evidence that the package was able to give verifiable data.

There was generally an excellent agreement of the results from the environmental-exploration package with literature values as shown for several well-characterized geochemical reference materials. Its usefulness in determining transition metals,

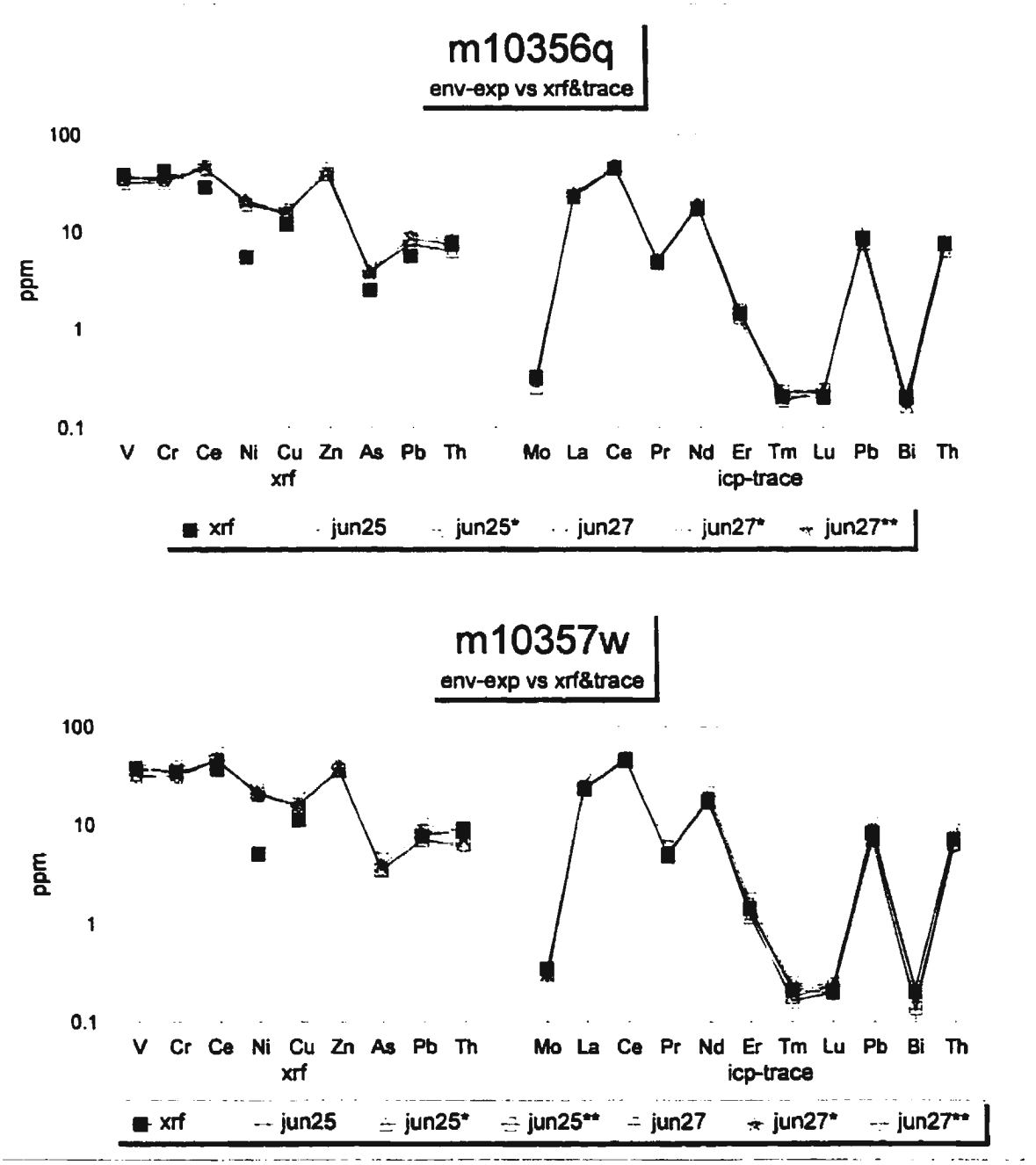

Fig. 4.8. Plot of results from proposed in-house reference material (designated as m10356q and m10357w) for elements common to ICP-MS env-exp and XRF trace, and ICP-MS env-exp and ICP-MS trace. Replicate analysis in ICP-MS env-exp designated by run names.

particularly the first-row transition elements, has been shown. More runs should, however, be performed to better identify the instrument parameters that would give a more reasonable compromise between sensitivity and the generation of oxide species and other polyatomic ions that would in turn be more adaptable to the varied types of matrices expected in typical environmental and exploration work. Fine tuning of oxide interference factors should be done as the exercise described here has shown that there were negative factors derived although this was more likely a result of the very high blanks for Ni and sometimes Cu which reached even thousands of counts. Further examination of compromises should be made, for example, in the use of higher solution concentrations but not high enough to trip the instrument's detector mode from pulse counting to analogue. The improvements in sample handling, digestion and other analytical procedures mentioned earlier would certainly be to the benefit of transition metal analysis as these would greatly reduce blank concentrations.

The analyses described here were started soon after the MUN SCIEX ICP-MS began to develop some problems of old age in its electronic circuitry and in other hardware components. The use of the VG did not produce better results as shown by the non-improvement in detection limits. It would have been ideal to perform further analyses on these geochemical reference materials if the opportunity existed, however, the time was indeed restricted by many factors, e.g., analytical work load, scheduling, and other factors. Nevertheless, the results presented here were sufficient to indicate that the ICP-MS environmental-exploration package was capable of reproducing published or previous

results.

The surrogate calibration for Sn-Sb should be tested further; likewise those for W-Lu and Pb-Hg should also be reviewed. There is a chance that the W-Lu calibration can still be established as shown on a per run basis. The fact that the calibration worked for Sn-Sb showed that the calibration itself was not the reason for not obtaining a sensitivity factor for Pb-Hg. For Hg, it was noted by McLaren *et al.* (1988) that a different sample digest procedure would be appropriate for its determination as Hg is most likely lost to volatilization. This matter should be studied further because of the element's importance in environmental as well as exploration work. Even for the elements Cd and Ag, analysis of samples that are known to contain significant concentrations of these elements may be needed to better quantify the results described here.

Chapter 5

Application of the High Pressure Digestion Technique and the Environmental-Exploration Package to the ICP-MS Analysis of Urban Stream Sediments and Soils from Cebu, Philippines

5.1 Introduction

Geochemical analysis of sediments and sedimentary rocks has diverse applications ranging from petrogenetic studies, through mineral deposit modelling, to investigations dealing with environmental concerns. Its importance in characterizing provenance types and determining secular variations in crustal composition has led to better understanding of the Earth's evolution (Taylor and McLennan, 1985). In the area of mineral exploration, sediment analysis has remained an integral part of routine geochemical prospecting as it constitutes a major first-pass method in evaluating an area's mineral potential (Rose *et al.*, 1979; Fletcher, 1981). Its utility in depicting broad scaled geochemical landscapes is exemplified in national geochemical programmes such as those conducted in Canada (e.g., Garrett *et al.*, 1990), England and Wales (Webb *et al.*, 1978), and Finland (Salminen and Tarvainen, 1995). This latter work in Finland was part of the transformation of a solely explorationist focus into one with increasing consideration of the relations and effects of the metals' presence to the environment and health. An expression of this turning point was the expansion of coverage in the publications of the Journal of Geochemical Exploration, following the formal recognition by the Association of Exploration Geochemists that environmental geochemists would be natural research partners to work

with as concerns about metal targets, analytical techniques, even pattern recognition and low detection limits are similar (Hoffman, 1989). Thereafter widening in scope is the application of sediment analysis as a tool in addressing environmental problems, working well with water analysis in studying the pathways, mobility, sources and sinks in the cycling of metals and other pollutants (Salomons and Förstner, 1984; Adriano, 1986; Förstner, 1989; Förstner *et al.*, 1990).

Other examples of the above-cited transformation are the works of the British Geological Survey in relating epidemiological studies to geochemical data (Thornton, 1983) and the subsequent application of geochemical data to problems in developing countries (Plant *et al.*, 1996); as are the works in Russia (e.g., Belogolova and Koval, 1995) and in Canada (e.g., the work in Newfoundland and Labrador by the Geological Survey of Canada, Davenport *et al.*, 1992). There is much information that can be gleaned from sediments and many analytical advances have stimulated detailed studies of very specific problems. The strategic information derived from baseline data, however, has produced additional data bases for comparison and valuable inputs for planning.

In this chapter, the high pressure digestion method discussed in Chapter 3 and the ICP-MS environmental-exploration package described in Chapter 4 are utilized in the analysis of urban stream sediments and soils from central Philippines. Although the sampled area may be classified to have a host of metal sources, it was not the objective of the present study

to pinpoint the specific sources but rather to arrive at an estimation of the current geochemical landscape where these types of potential pollution sources exist.

5.2. Urban Stream Sediments and Soils

5.2.1. Description of the Study Area

The samples come from a metropolitan area in Cebu island, central Philippines located at approximately 10 ° N and 124 ° E (Fig. 5.1). The underlying rocks in the area belong to a young (Pliocene-Pleistocene) unit composed of calcarenite, limestone and minor marl, overlain by Recent alluvium (Fig. 5.2). This young limestone unit similarly underlies the smaller island (Mactan) adjacent to the central bulge of Cebu island. In Mactan island, the limestone is marked by pockets of alluvial material deposited along small depressions in a karstic terrain.

The metropolis consists of 3 cities and 6 municipalities and represents a fast expanding center in the country. The stream sediment samples were from the cities of Cebu and Mandaue, both on Cebu island, within an area of approximately 50 km^2, while the soil samples were from Lapulapu City across the channel on Mactan island (Fig. 5.3). Five rivers flow through the 2 cities from the watershed line not more than 10 or 12 km to the NW, emptying into the narrow channel. Seven samples (labeled A-series) were included with the stream sediments but were actually from recently constructed drainage channels

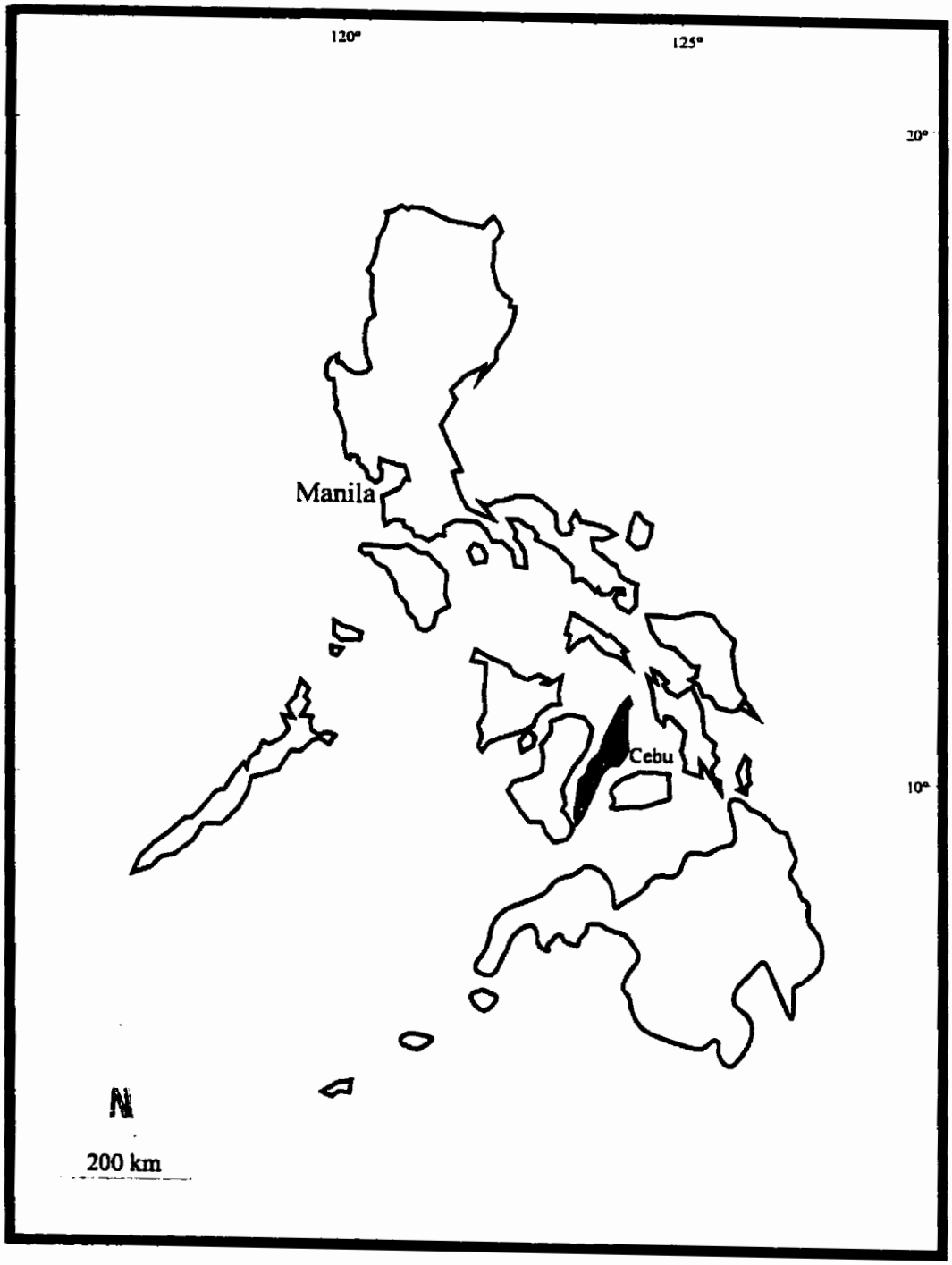

Fig. 5.1. Location map of Cebu island (shaded), Philippines. The island is about 600 km south of the capital, Manila.

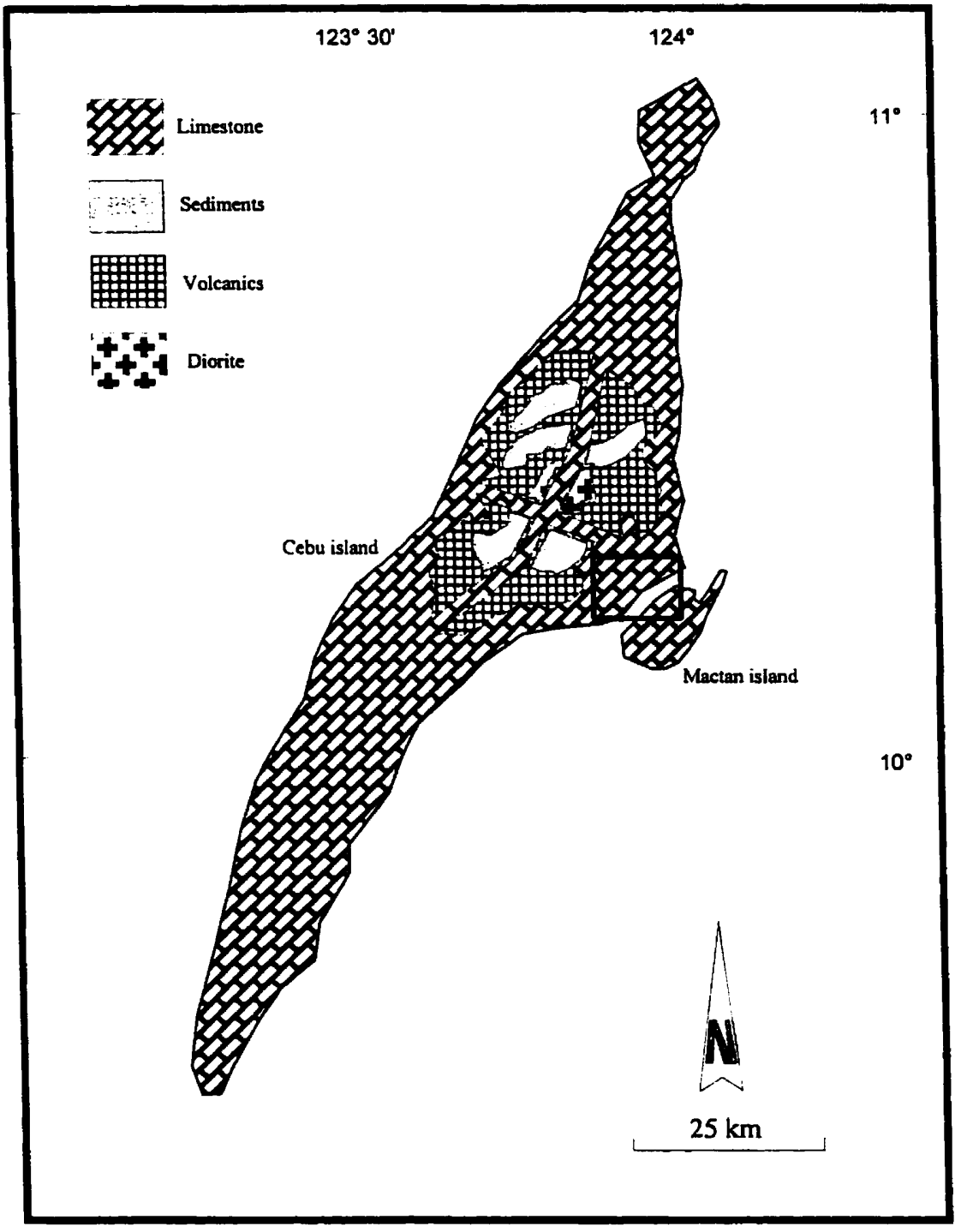

Fig. 5.2. Simplified geologic map of Cebu island and Mactan island, Philippines. Box indicates study area of Metro Cebu, which is underlain by young limestone.

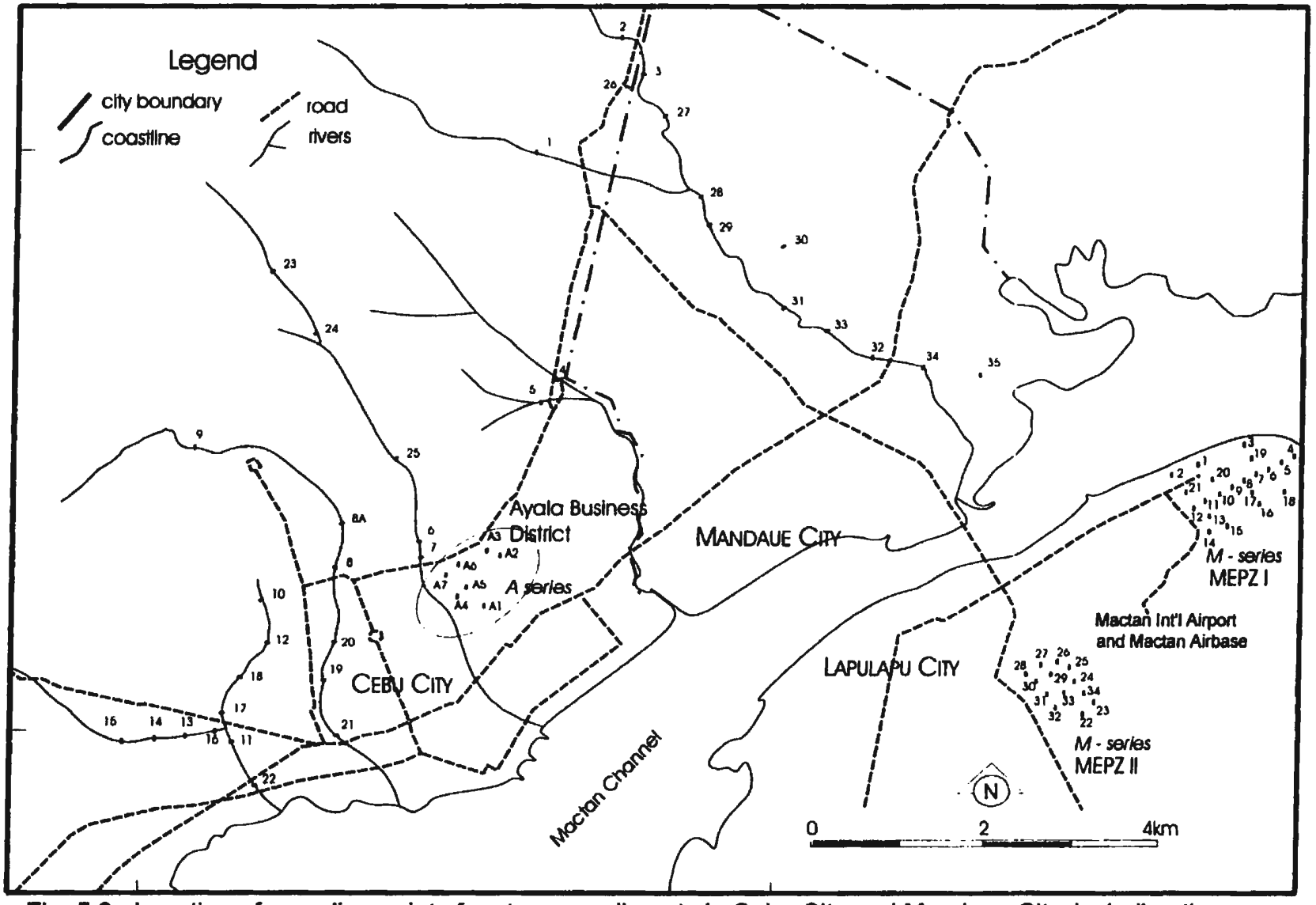

Fig. 5.3. Location of sampling points for stream sediments in Cebu City and Mandaue City, including the A-series samples from Ayala district, and soil samples in Lapulapu City (M-series) from MEPZ I and II.

laid out within a large commercial center undergoing development (Ayala Business District).

Land-use zoning in Cebu and Mandaue Cities classifies the area into 6 categories: residential, commercial, industrial, agro-industrial, parks and open spaces, and watershed (Fig. 5.4) (CCGC, 1992; MCPO, 1982). Exemptions to designated types of utilization as well as the general social encouragement of backyard industries have allowed small industrial operations within residential or commercial zones. Some of the heavy metal point sources in these 2 cities are small-scale iron and steel works and foundries, metal finishing plants, and medium-scale vehicle assembly and parts manufacturing operation, and agricultural fertilizer manufacturing. Non-point sources are the residential and commercial zones because of domestic sewage, and transportation corridors, aside from the formal industrial areas.

The soil sampling sites in Lapulapu City were within 2 areas, of about 2 and1 km^2 respectively, designated by the Philippine export processing zone authority specially for light to medium industries ranging from aircraft parts manufacturing, silicon chip assembly, metal finishing, plastic industrial products, electronics, processed steel parts, etc. The 2 areas are referred to as MEPZ I and MEPZ II, the former being in existence for about 30 years and is the site of approximately 70 companies while the latter is an expansion area generally at the early stage of land development with 3 establishments undergoing construction at the time of sampling. These 2 areas are about 2 km apart.

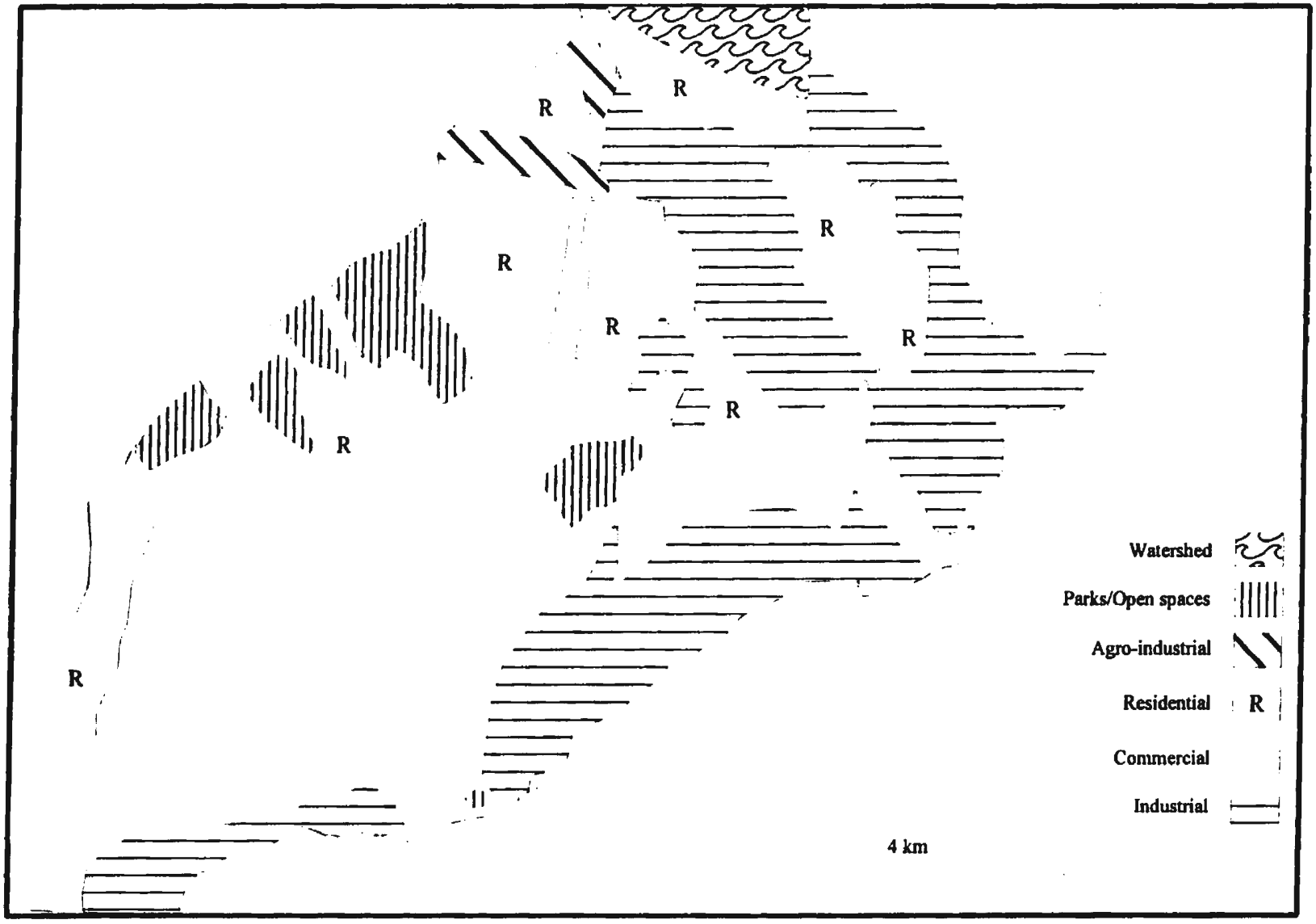

Fig. 5.4. Combined land use zones in Cebu City and Mandaue City, Philippines.

5.2.2. Sampling Method

Bulk stream sediments weighing approximately 5 to 7 kg when wet were collected in the field using polyethylene (PE) scoops and placed in pre-numbered, resealable PE bags. Every effort was made to have the sampling sites uniformly distributed throughout the target area, however, actual conditions and accessibility problems in many sites limited the number of locations finally sampled. The soil samples, on the other hand, were obtained along a grid covering the sub-areas. These were collected from holes dug with plastic spades down to about 20 to 25 cm (generally to B-horizon) and manually cleared of large organic debris such as roots of plants and buried leaves. Samples were of similar weights as the stream sediments and collected in a similar manner. Sediment and soil samples were air-dried at room temperature at the sample preparation room of the Mines and Geosciences Bureau compound in Mandaue City. Care was exercised in avoiding contamination from other samples present in the drying area and in the use of proper handling procedures.

Dried samples were not crushed but only disaggregated using a ceramic mortar-and-pestle and passed through nylon-meshed sieves of 1.41 mm, 595 μm, 177 μm and 149 μm. Each size fraction was weighed. The smallest size fractions (< 149 μm) were brought to Memorial University for analysis. These samples were then re-sieved through 88 μm nylon screens and both resulting fractions weighed. Results reported below were from the

analysis of the <88 μm fraction. A total of 43 stream sediment and 34 soil samples were prepared for analysis.

5.3. Experimental

5.3.1. Sample Preparation

Sample digestion preparatory to ICP-MS analysis was conducted using the high pressure technique described in Chapter 3. Briefly, 0.1 g of sample was placed in a high pressure teflon digestion vessel (HPDV), after which 3 ml of 8 N HNO_3 and 2 ml of HF were added. After placing the lid on the vessel, the whole set (6 bombs per set) was assembled and placed at 180 ° C in a conventional drying oven overnight. The assembly was then removed from the oven and allowed to cool and after taking off and rinsing the lid, the vessel was set on a hotplate at 70 ° C and the samples were evaporated to dryness. Two ml of 8 N HNO_3 and 1 ml 2.8% boric acid were added and allowed to fume to dryness. The boric acid was added to complex the free F^- ions resulting from the addition of HF. A second addition of 2 ml of 8 N HNO_3 was made and likewise evaporated to dryness. Then about 2 ml of 8 N HNO_3 were added and the lid replaced and the vessel was warmed gently to dissolve the residue. Solution was transferred to a clean 120 ml polypropylene bottle, rinsing the HP vessel and cover with nanopure water. To this were added 0.665 ml HF/boric acid solution (0.1 M HF, 0.453 M boric acid) and 1.35 ml oxalic acid (0.222 M), then made up to final weight of 60 g with nanopure water.

5.3.2. Inductively Coupled Plasma-Mass Spectrometric Analysis

The sample solutions were analyzed using the environmental-exploration (ICP-MS env-exp) package described in Chapter 4. Measurement was made on the following analytical masses: ^{51}V, ^{52}Cr, ^{55}Mn, ^{59}Co, ^{60}Ni, ^{65}Cu, ^{66}Zn, ^{75}As, ^{98}Mo, ^{107}Ag, ^{111}Cd, ^{118}Sn, ^{121}Sb, ^{139}La, ^{140}Ce, ^{141}Pr, ^{145}Nd, ^{167}Er, ^{169}Tm, ^{175}Lu, ^{208}Pb, ^{209}Bi, ^{232}Th; ^{238}U and $^{238}U^{16}O$ were measured to monitor polyatomic ion formation. The sample solutions were also analyzed using the ICP-MS trace package developed in the Department of Earth Sciences, Memorial University (Jenner *et al.*, 1990; Longerich *et al.*, 1993) and briefly described in Sec. 3.3.4. The masses measured were ^{7}Li, ^{85}Rb, ^{86}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{95}Mo, ^{133}Cs, ^{137}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{145}Nd, ^{147}Sm, ^{151}Eu, ^{159}Tb, ^{160}Gd, ^{163}Dy, ^{165}Ho, ^{167}Er, ^{169}Tm, ^{173}Yb, ^{175}Lu, ^{177}Hf, ^{181}Ta, ^{203}Tl, ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{209}Bi, ^{232}Th; with ^{238}U (and $^{238}U^{16}O$) as oxide monitor.

5.3.3. X-ray Fluorescence Spectrometry

As a matter of routine laboratory procedure at the Department of Earth Sciences, Memorial University of Newfoundland, samples submitted for ICP-MS trace analysis undergo analysis by x-ray fluorescence spectrometry (XRF) as a means of controlling and assuring the quality of data and/or identifying matrix composition. The <74 μm fraction of the sediment and soil samples from Cebu, Philippines were also submitted for XRF

analysis, although pressed pellets were made for only 62 samples (36 stream sediments and 26 soils) out of the 77 because of insufficient weight for 15 samples. The procedure followed that described in Longerich (1995) changing sample size from 5.0 g to 3.0 g. The amount of resin used was changed accordingly to maintain a similar sample to resin ratio. In a 100 ml glass jar were placed 3.0 g of sample and 0.42 g of BRP-5933 Bakelite phenolic resin (Bakelite Thermosets, Brampton, Ontario, Canada). Two 0.5 in (1.27 cm) diameter stainless steel ball bearings were added and a plastic lid attached. The jar was placed on a roller mixer for approximately 10 minutes to mix the sample and resin thoroughly. The mixed powder was placed in a Herzog (Germany) pellet press (29 mm diam mould) and pressed for 5 s at a pressure of 20 tonnes. The pellets were then placed in an oven at 200 ° C for 15 minutes.

Data were obtained using a Fisons/ARL (Applied Research Laboratories, Mississauga, Ontario, Canada) model 8420+ sequential wavelength dispersive X-ray spectrometer. Data acquisition parameters are given in Longerich (1995). Data were acquired for 30 analytes (elements and oxides) and a regular run would include 27 backgrounds and the Rh Kα Compton peak. The sequence going into the spectrometer was 6 reference materials (DTS-1, BHVO-1, SY-2, SY-3, SiO_2 and PACS-1), 8 samples, 6 reference materials (as above), 8 samples, 6 reference materials (as above), 8 samples, 6 reference materials (as above). Four quality control reference materials (AGV-1, DNC-1, JG-2, and BCR-1) were analyzed as unknown samples. Data acquisition times varied from 4 to 100 s based on sensitivity of analyte emissions and typical silicate geological material abundance of the

various elements. Procedures to correct for background, interferences and matrix effects together with sensitivity calibration are discussed in Longerich (1995).

5.4. Accuracy and Precision

Measure of accuracy was discussed in Section 4.10 which compared the results for several international geochemical reference materials (using the ICP-MS env-exp package) with compiled values (*e.g.*, from Govindaraju, 1989). These GRMs were PACS-1, MESS-2, HISS-1 from NRCC, BSK-1, AGV-1, BCR-2, DNC-1, G-2 from USGS, NBS-688 from NIST, MRG-1, SY-2, SY-3 from CCRMP, and JB-1a from GSJ. It was shown that for the elements V, Co, Cr, Ni, Sn and Sb, there was acceptable agreement between the data and the literature values. Copper, Zn, Mo and Pb gave reasonable agreement. Acceptable results for As and Cd were shown for the geochemical reference materials PACS-1 and MESS-2 but for the other GRMs, the data for Cd, As and Ag were generally near detection limits.

In the ICP-MS environmental-exploration runs that contained the sediment and soil samples, the results for the GRMs PACS-1 and MESS-2 indicated good agreement with literature values. This relationship was shown for the elements V, Cr, Cu, Zn, As, Mo, Cd, Sn, Sb and Pb (Fig. 5.5). Nickel, however, did not produce a good correlation between the experimental and literature values because of the high blanks in the last 2 runs (out of the 3 performed in the VG PlasmaQuad) although there was initially a reasonable

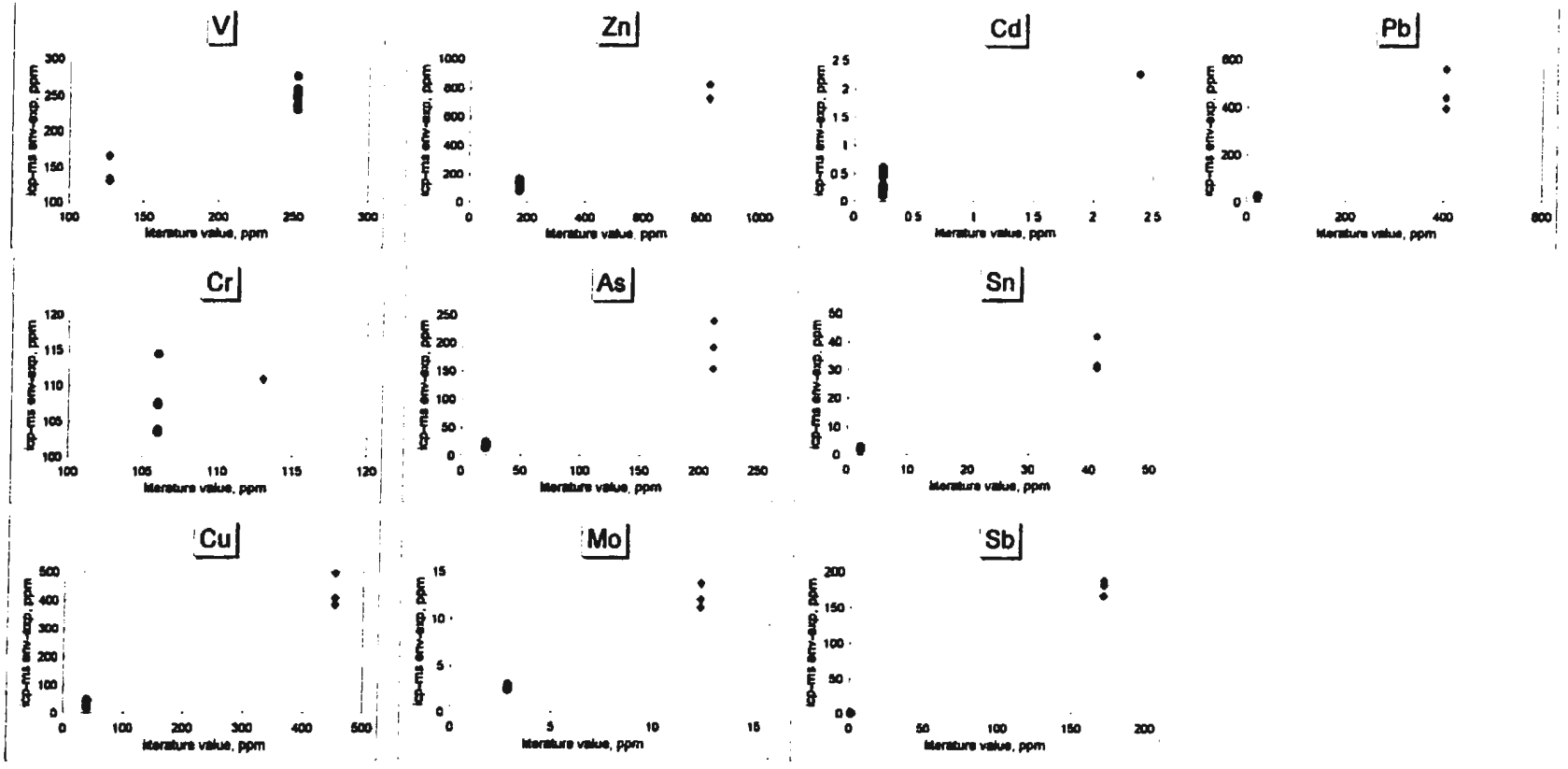

Fig. 5.5. Comparison of results from ICP-MS env-exp package with literature values for V, Cr, Cu, Zn, As, Mo, Cd, Sn, Sb and Pb for the GRMs PACS-1 (diamonds) and MESS-2 (circles).

agreement with literature values in the earlier runs (up to run Nov28107 which was the first run performed in the VG after switching from the SCIEX ELAN).

Some sample solutions were duplicated in each run to provide a measure of instrumental replicability of the method under study. Table 5.1 shows the averages of the relative standard deviations calculated for each duplicate pair in the ICP-MS environmental-exploration runs. Duplicate analysis gave less than 10% RSD for the elements V, Cr, Mn, Co, Cu, Mo, Sn, Sb, La, Ce, Pr, Nd, Er, Tm, Lu, Pb and Th. Somewhat poorer precision was shown by Zn (19%), As (27%), Ag (19%), Cd (26%), Bi (12%). Cadmium RSD would actually increase to 66% if the duplicate pair that gave 706% RSD was included. This particular pair gave a mean of 0.03 ppm Cd, with 0.18 ppm standard deviation, values that are below the detection limit of 0.4 ppm for that run (Jan29108). Nickel RSD in the duplicate pairs averaged 17% for the first 6 sets of duplicates until the subsequent runs gave highly erratic Ni values (due to high blanks). It was decided that the Ni results from the XRF analysis would be used in the discussion of the geochemical landscape below.

Results for some of these duplicate pairs, mostly GRMs and the proposed MUN in-house reference material (replicates M10356Q and M10357W), are graphically shown in Fig. 5.6 where the mean of the duplicate pairs' measured concentration was compared with the corresponding RSD of that pair. Figure 5.6 plots 7 of the pairs included in run Jun27107, and it is indicated that the higher RSDs for Bi, Cd, Ag and Mo coincide with lower

Table 5.1. Average relative standard deviation of the elements for 18 duplicate pairs in the 5 runs that contained the sediment and soil samples from Cebu, Philippines.

Element	RSD, %	Element	RSD, %	Element	RSD, %
V	5	Mo	10	Nd	4
Cr	7	Ag	19	Er	6
Mn	5	Cd	26	Tm	7
Co	6	Sn	3	Lu	6
Ni	17 (5 pairs)	Sb	4	Pb	7
Cu	10	La	3	Bi	12
Zn	19	Ce	3	Th	5
As	27	Pr	4		

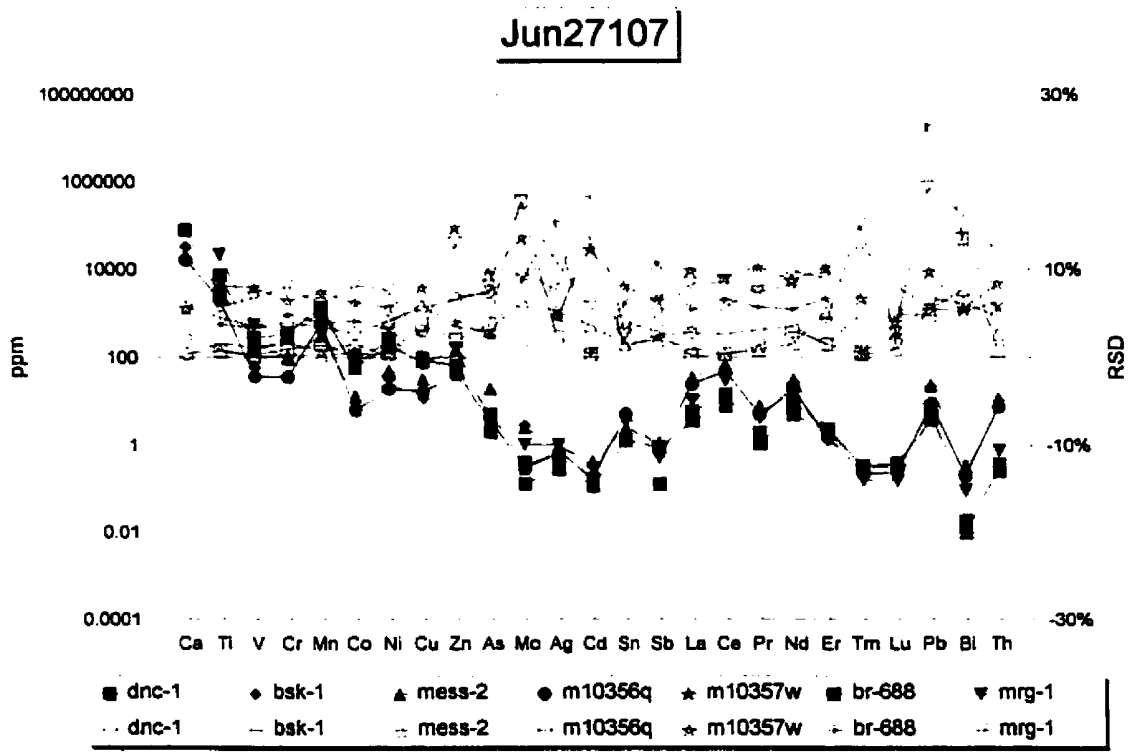

Fig. 5.6. Mean element concentration in ppm (filled symbols, refer to left axis) and RSDs in % (open symbols, refer to right axis) of 7 duplicate pairs in the Jun27107 ICP-MS env-exp run. The higher RSDs of Mo, Ag, Cd and Bi were from values less than or near D.L. The pairs are 5 GRMs and 2 replicates of in-house reference material.

concentration of the element in the sample. This observation, that as the concentration approaches detection limits, the relative difference between replicates becomes proportionately larger, was typical in most runs. The detection limits for these elements in run Jun27107 were 0.023 ppm (Mo), 0.043 (Ag), 0.050 ppm (Cd) and 0.024 ppm (Bi). Lead RSD was similarly high in 2 of these duplicate pairs although the concentrations in the pairs were well above the detection limit. This was also indicated by Zn in the pairs M10356Q and MRG-1. The behavior of Pb was most likely due to contamination in the laboratory from improper sample solution handling as opposed to a particulate air source of Pb since only 2 of the pairs were high. The other 5 pairs gave RSDs of less than 10%.

Elements with the higher concentrations, Ca and Ti, were included in the plot to show that as the concentration increases, the RSDs tend to become smaller. This was also indicated for 7 other duplicate pairs in the same run (Fig. 5.7). Calcium and Ti had less than 5% RSD with Ca and Ti concentration at around the 1 percent level. The high RSDs for Bi and Cd with accompanying low concentrations (near detection limit) were similarly evident for this group of duplicate pairs. One pair had Cu at negative RSD due to high blank concentration that masked the low measured Cu value in that sample. Most of the other elements, however, had RSDs less than 10% including the REEs, which showed good precision even at low concentration in the sample (Fig. 5.6).

The measure of accuracy of the ICP-MS environmental-exploration package described earlier in Section 4.10, which compared the results for several international GRMs with

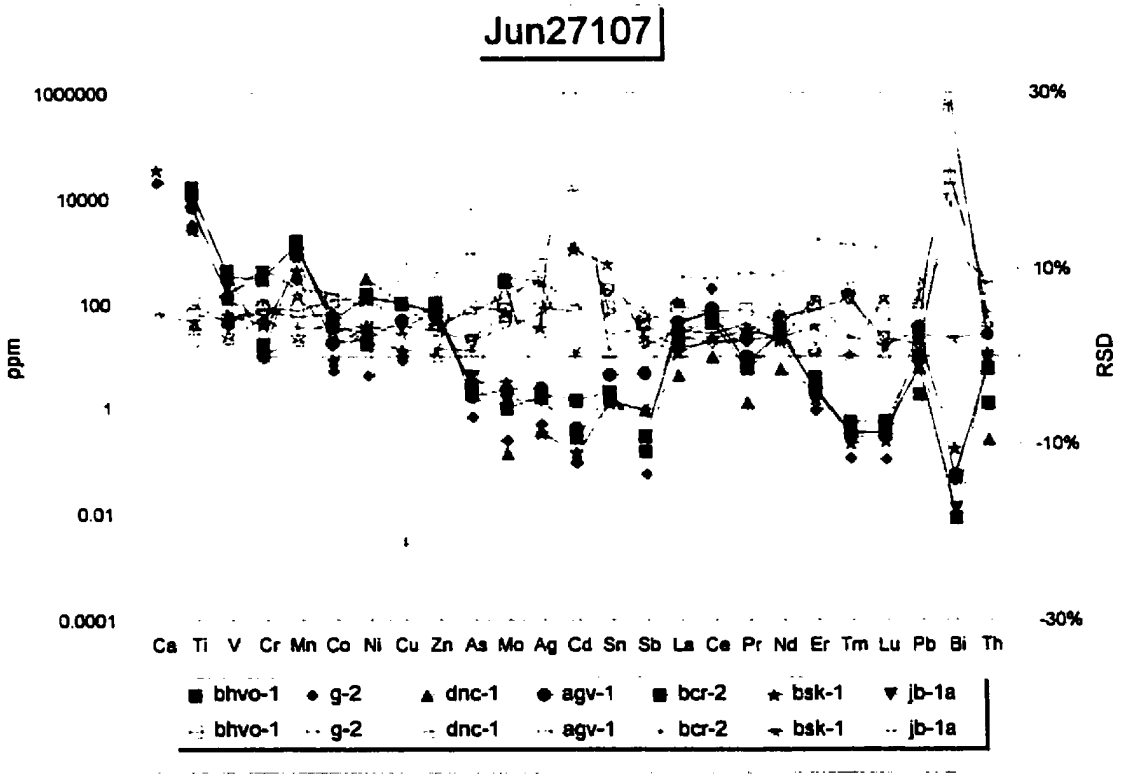

Fig. 5.7. Mean element concentration in ppm (filled symbols, refer to left axis) and RSDs in % (open symbols, refer to right axis) of 7 duplicate pairs in the Jun27107 ICP-MS env-exp run. The higher RSDs of Cd and Bi were from values less than or near D.L. The large Cu RSD was due to high blank concentration. The pairs are all GRMs.

literature values, demonstrated good agreement for the elements V, Co, Cr, Ni, Sn and Sb, and reasonable agreement for Cu, Zn, Mo and Pb. Results from the duplicate pairs described in this section indicated good precision for most elements, except for those with values near or below detection limit (Bi, Cd, Ag and Mo) and those that were likely affected by contamination during analysis or sample preparation (Pb and less likely for Zn). With these measures, the ICP-MS environmental-exploration package was shown to be capable of performing well in terms of accuracy and precision.

5.5. Comparison of Results from Environmental-Exploration Package with those of other Memorial University of Newfoundland Trace Methods

5.5.1. Inductively Coupled Plasma-Mass Spectrometry Environmental-Exploration Package and Inductively Coupled Plasma-Mass Spectrometry Trace Package

The ICP-MS trace package developed by the Earth Science Department of Memorial University has been demonstrated to produce good and/or excellent accuracy and precision for 26 elements in the analysis of USGS reference materials (Longerich *et al.*, 1990; Jenner *et al.*, 1990). The results using this package were compared with those from the ICP-MS env-exp.

Ten elements are common to both packages: 7 rare-earth elements (La, Ce, Pr, Nd, Er, Tm, Lu) with Pb, Bi and Th. Figure 5.8 shows XY plots for these elements (ppm data from both ICP-MS packages) and the corresponding correlation coefficients for the sediment and soil data from Cebu, Philippines. Wider bands about the 1 : 1 line are

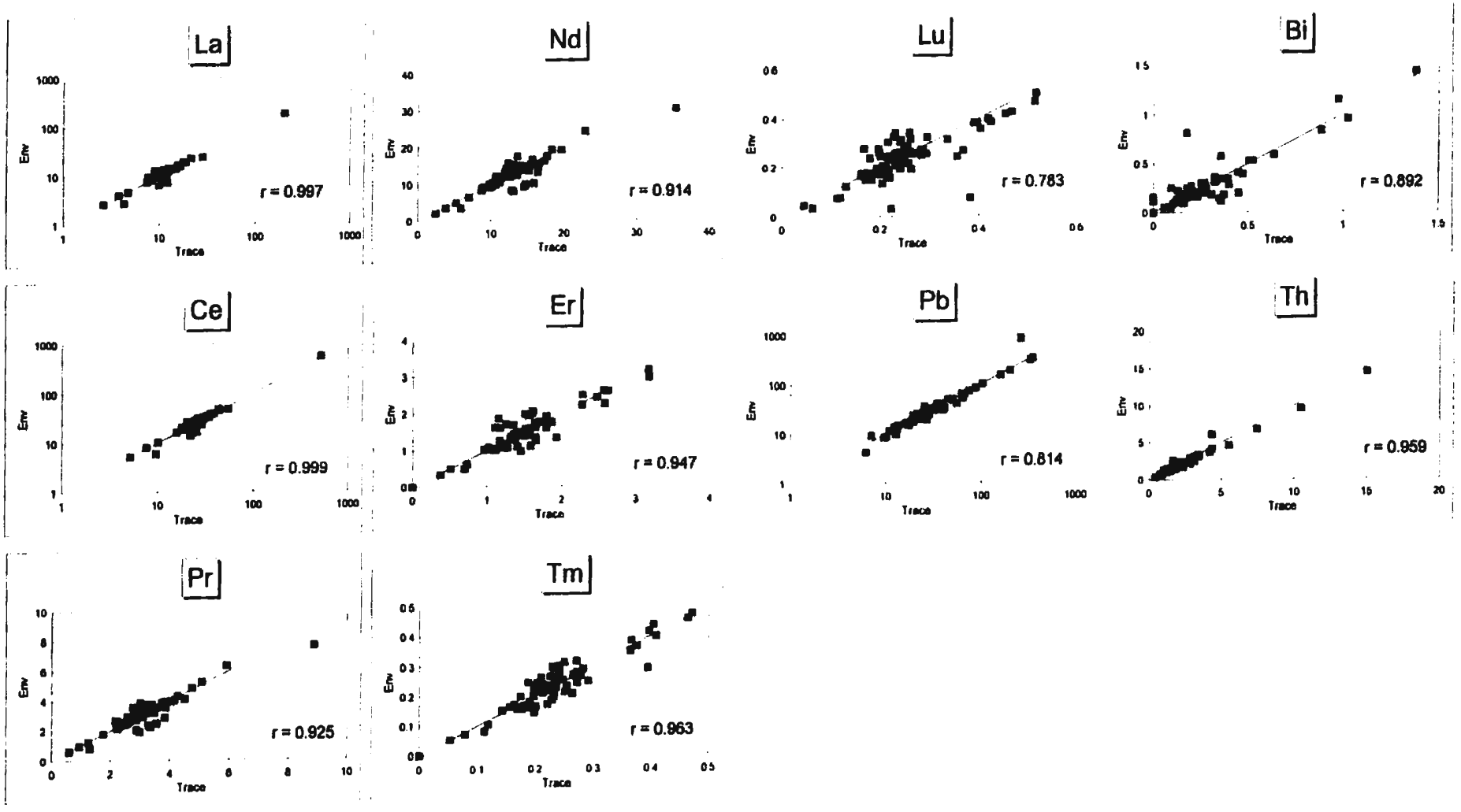

Fig. 5.8. XY plots for La, Ce, Pr, Nd, Er, Tm, Lu, Pb, Bi and Th from stream sediments and soils using ICP-MS trace and env-exp packages indicating good agreement and a high correlation coefficient.

exhibited by the elements Er, Tm and Lu, nevertheless, good correlation is displayed by the data points for all elements. Even with one or two outlying data points for Lu, Pb and Bi, the correlation coefficients derived for these paired data sets gave a high range from r = 0.783 (Lu) to 0.999 (Ce). For these common elements, the ICP-MS environmental-exploration package showed good conformity with the MUN ICP-MS trace package, demonstrating that the ICP-MS environmental-exploration package is similarly capable of producing good and/or excellent accuracy and precision as the MUN ICP-MS trace package.

5.5.2. Inductively Coupled Plasma-Mass Spectrometry Environmental-Exploration Package and X-ray Fluorescence Spectrometry

X-ray fluorescence spectrometry is one of the most widely used routine instrumental methods of analyzing rock samples for the major elements Na, Mg, Al, Si, P, K, Ca, Ti, Mn, Fe and the trace elements Rb, Sr, Y, Nb, Zr, Cr, Ni, Cu, Zn, Ga, Ba, Pb, Th and U (Fletcher, 1981; Potts, 1987). The results of analyses of the sediment and soil samples from Cebu, Philippines using the ICP-MS environmental-exploration package were compared with the results from XRF for the 7 elements common to both methods: V, Cr, Ni, Cu, Zn, As and Pb.

Good agreement is shown in Fig. 5.9 for the elements V, Cr, Zn and Pb with the data spanning 2 orders of magnitude, and for Cu across 3 orders of magnitude. This agreement

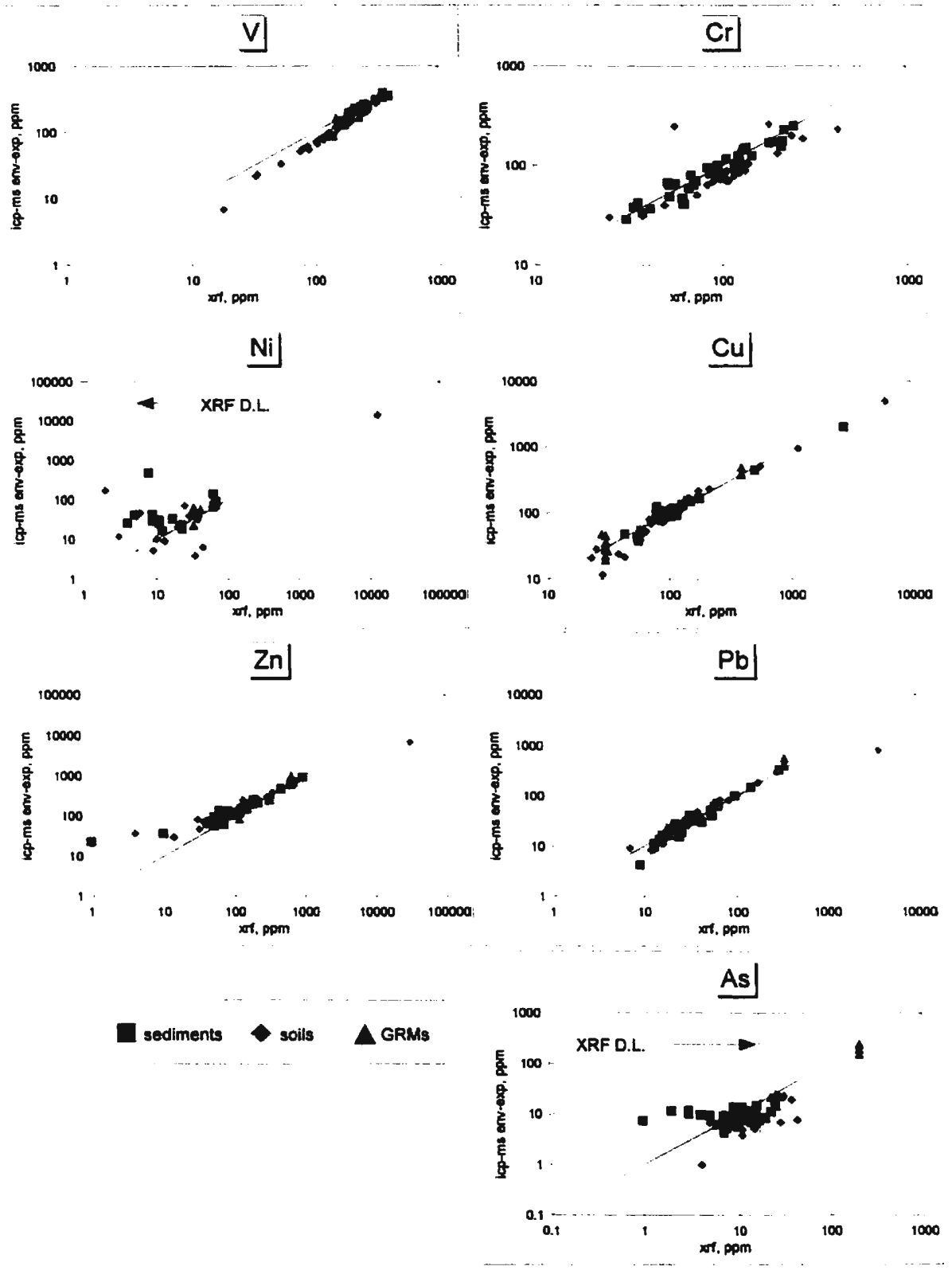

Fig. 5.9. XY plots comparing results from XRF and ICP-MS env-exp package for V, Cr, Ni, Cu, Zn, Pb and As from sediment and soil samples from Cebu, Philippines, and the GRMs MESS-2 and PACS-1.

is shown for the 3 sample types analyzed: sediments, soils, and geochemical reference materials.

The trend near the lower end of the scale for V shows ICP-MS environmental-exploration results to be consistently lower than those from XRF. The discrepancy at the ends of the data range was also shown for Zn where the ICP-MS environmental-exploration package gave a lower value than the XRF at the upper end (for a lone outlier), while it gave higher values at the lower end (for several samples). It is possible that the discrepancy accompanying the high outlier may be due to the value being out of calibration range for the XRF. The reference material used to calibrate Zn signals in the XRF is BHVO-1 with a published concentration of 101 ppm Zn. The sample in question in the present set of data has a Zn value in the thousands (6,730 ppm using ICP-MS; 31,256 ppm using XRF). It is believed that with the ICP-MS having the advantage of a long linear dynamic range, the result from this method is more accurate than that from the XRF for this particular sample. This also seems to be the case for one high outlier in the Pb data, the sample giving 810 ppm using ICP-MS and 3,726 ppm using XRF. The reference material used to calibrate Pb in the XRF is SY-2 with 86 ppm. The disagreement in the lower end of the data scale for Zn may also reflect the XRF's inherent background problems.

Good agreement between ICP-MS environmental-exploration and XRF values was not shown for the elements Ni and As (Fig. 5.9). Although the data points become diffused as they approach detection limits (XRF detection limit for Ni about 5 ppm and for As about

15 ppm), arsenic may have also been affected by loss because of its volatility during the ICP-MS sample digestion phase. It is interesting to note, however, that while the data for the sediments appear to show no correspondence between the methods used, the GRMs display good agreement and the results for the soil samples were in reasonably good agreement. The better correspondence shown for the geochemical reference materials may be indicating better dissolution of this matrix type as influenced conceivably by particle size of the original sample powder. This influence by particle size is further discussed below in the following section.

For Ni, the results for the geochemical reference materials were good but those for the soil samples do not give good correspondence between the ICP-MS environmental-exploration package and XRF. The results for the sediment samples appear to indicate agreement between the methods but only for data points that plotted above zero. As mentioned earlier in Sec 4.7 and Sec. 4.10, most samples gave negative values due to the calibration blanks having high Ni backgrounds. It was discussed in Chapter 4 that this behaviour of Ni was most likely due to memory effects that have been noted in the ICP-MS. Along with the poor accuracy for this element in these runs, as also mentioned above (Sec. 5.4), this has necessitated the use of XRF results for the metal in further discussions of field distribution. For future analysis using the ICP-MS environmental-exploration package in instruments and settings similar to those used in this study, increasing the wash times may be necessary to minimize memory effects for this metal.

5.6. Particle Size Effect

The geochemical reference materials gave good correspondence between ICP-MS environmental-exploration and XRF for Ni and As. In contrast, the sediment samples appear to have no correspondence between these two methods especially for As. It should be recalled in Sec. 5.3.1. that the sample preparation of the sediments and soils involved only sizing and sieving through a series of screens (sieve sizes 1.41 mm, 595 μm, 177 μm, 149 μm) until the final size of < 88 μm was obtained. No further crushing or grinding (only disaggregating) was done after air-drying of samples. This was done to obtain only the fine fraction of the sediment and soil samples which was the likely compartment where mobilized elements would reside. On the other hand, most GRMs are described to undergo grinding using typical mills to pass a fine mesh size. Sample preparation for the reference materials HISS-1, MESS-2 and PACS-1 involved sieving through a No. 120 (125 μm) screen (NRCC, 1995). Although the reference screens used are commonly of No. 200 (74 μm) size, it is certain that majority of the particles that pass through are significantly finer than 74 μm. This can be observed in the preparation of rock samples at the Department of Earth Sciences, Memorial University, where crushing and grinding of samples always produce a fine powder although samples are not sieved.

Size analysis was done on 4 samples to examine the differences in particle size among the sample types at hand. These samples comprised 2 geochemical reference materials (HISS-1 and MESS-2), one stream sediment sample (lab no. M12912X; field no. UGC-3), and

one soil sample (lab no. M12954I; field no. UGC-M9). UGC-3 was taken from the northernmost stream in the study area within a 15 m wide portion (active channel 5 m wide), at a time when water flow was low. Both banks were alluvial and there were abundant silt-sized material along the active stream bed. UGC-M9 is a soil sample collected from MEPZ-I specifically from a landscaped lawn outside the gates of a manufacturing building adjacent to the main thoroughfare. It is expected that there would be some variation in the particle size distribution among the sediment and soil samples collected from the Philippines, however, the difference would not be of a large magnitude as these samples were pre-sieved through 149 μm size screens before bringing them to MUN. HISS-1 and MESS-2 are geochemical reference materials from NRCC (1997); the first from the Hibernia Shelf off the coast of Newfoundland, while the second was from the Beaufort Sea. Table 5.2 gives the results from the size analysis done using 3 sieve sizes (88 μm, 62.5 μm and 53 μm) from the Sedimentology Unit of MUN Earth Sciences.

HISS-1 was indicated to have the most amount of fines and MESS-2 the least amount of coarser particles among the 4 samples. MESS-2 was a close second to HISS-1 in the amount of fine particles with 38% of the total passing through the 53 μm screen. There was even a bit of caking of material for MESS-2 and HISS-1 that formed around the edges of the sieve (for 88 μm and 62.5 μm) indicative of moisture content that held the particles together and prevented them from disaggregating properly. This material was, however, lesser for MESS-2 compared with HISS-1. No caking of material took place in the stream sediment (M12912X) nor in the soil (M12954I) sample. Another observation

Table 5.2. Weights and percentages of size fractions of HISS-1, MESS-2, M12912X and M12954I that passed through the 88 μm, 62.5 μm and 53 μm sized sieves.

Sieve size opening	HISS-1	MESS-2	M12912X	M12954I
88 μm (g)	0.574	0.076	0.174	0.187
62.5 μm (g)	0.302	1.196	1.787	1.595
53 μm (g)	1.586	0.793	0.644	0.861
Total	2.462	2.065	2.605	2.643
88 μm (%)	23.31%	3.69%	6.68%	7.08%
62.5 μm (%)	12.28%	57.92%	68.60%	60.35%
53 μm (%)	64.41%	38.39%	24.72%	32.58%
Total	100.00%	100.00%	100.00%	100.00%

was that material from MESS-2 and HISS-1 did not settle as quickly as those of the stream sediment and soil samples, signifying further that the GRMs contain a greater amount of fines. Preparation of the geochemical reference materials PACS-1 and MESS-2 is said to involve no grinding and the material was passed only through 120 μm size screens (NRCC, 1995). Nevertheless, these are marine sediment samples and it is highly likely that the percentage of fines in their respective sources is much greater than in fluvial systems. Clastic dispersion favors the deposition of clay sized material in open ocean basins and processes leading to the formation of authigenic clay are common at the seawater-sediment interface (Chamley, 1997). This assures the preponderance of the fine grain size fraction in the above reference materials.

A most probable reason why the the soils appear to have a better As correspondence between methods than the stream sediments may be due similarly to particle size difference between these 2 sample matrices. In the study area, it is known that there is more clay-sized fraction in the soil compared to stream sediments. This is borne out by the relatively greater amount of <53 μm sized fragments in the soil sample M12954I compared to the stream sediment sample M12912X (Table 5.2). Soil development is characterized by clay mineral formation and the presence of Al- and Fe-hydroxides varies directly with the clay content of the soils (Pedro, 1997). Arsenic is said to follow the dominance of hydrous Al- and Fe-oxides (Adriano, 1986) and even for limestone-derived soils, the tendency to form Ca-arsenates would aid in retaining the metalloid in this matrix.

During the initial part of the study, 6 sediment samples that were among several brought earliest to MUN were used in a small experiment involving particle size. The XRF results described above were from the analysis of pellets made with the <88 μm fraction of the samples, but before sieving the sediment samples through the 88 μm screen, a small portion of the <149 μm fraction of the 6 samples was set aside after homogenization. Pressed pellets were also made for these and the coarse (minus 149 μm, plus 88μm) and fine (minus 88 μm) fractions were analyzed together in one XRF trace run.

Figure 5.10 is a XY plot of the 6 sediment samples comparing the two size fractions. There was no dramatic divergence in contents but all elements, except Rb and Ba, generally showed higher concentration in the minus 88 μm fraction than in the coarser fraction. This observation, which was indicated by Ni, Cu, Zn, Ga, Sr, Y, Zr, Nb and Pb, supports the generally accepted view regarding preference of trace elements to reside in the finer fraction. Zirconium and Y associate with the clay minerals enabling their widespread distribution in basins; Ga, Nb, together with first-row transition metals tend to be relatively immobile compared with the alkali and alkaline earth elements which are quite soluble during the early to intermediate stages of weathering (Taylor and McLennan, 1985).

The differing behaviour of Ba and Rb may be attributed to their affinity with calcareous fragments, although one would expect that Sr would be associated with this group as well. Association with the coarser fragments in the sediments, most probably limestone lithic

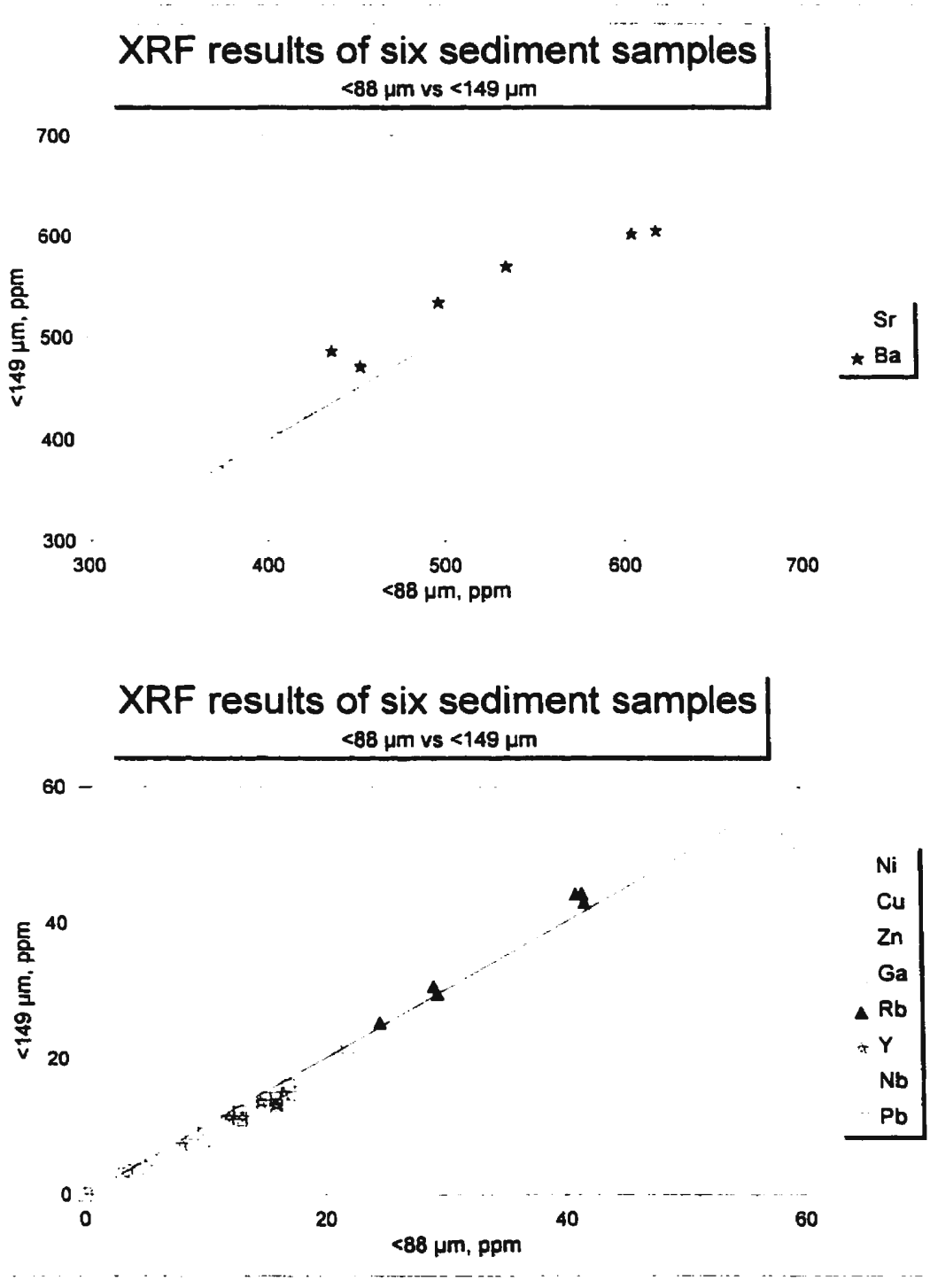

Fig. 5.10. XRF results for six stream sediment samples comparing < 88 µm and < 149 µm size fractions and indicating Ba and Rb to be higher in the coarser (< 149 µm) fraction.

fragments, may indicate the presence of some barium mineral interspersed in the limestone fragments. However, this limestone unit underlying the study area has not been shown to have barite in its stratigraphic sequence nor barite has been indicated in older rock formations (BMG, 1982). It is possible, although remote, that Ba occurs as a solid solution with Ca partitioned into calcite (Tesoriero and Pankow, 1996) but this does not explain the relative preference in the sediments. Its source could entirely be different altogether, e.g., from releases of anthropogenic sources.

This association is consistent with the general trend showing the difference in Rb and Ba content of the stream sediment and soil samples from the area (Fig. 5.11). It is clear that these elements are higher in the stream sediments compared with the soil samples. If the Ba were coming from barite minerals, the relatively harder and heavier barite mineral would most likely be retained in the coarser fraction of the sediments during mechanical erosion. Alternatively, Ba and Rb may be correlated with feldspars or less likely sphene (Cullers, 1988), which could indicate input from non-carbonate rocks exposed in the watersheds.

In summary, for most of the elements compared (V, Cr, Cu, Zn and Pb), there was good agreement between results from the ICP-MS environmental-exploration package and from x-ray fluorescence spectrometry in the analysis of the stream sediment and soil samples from the Philippines. This was not shown for As and Ni and it is likely that arsenic was lost during evaporation of the acids in the sample preparation for ICP-MS analysis.

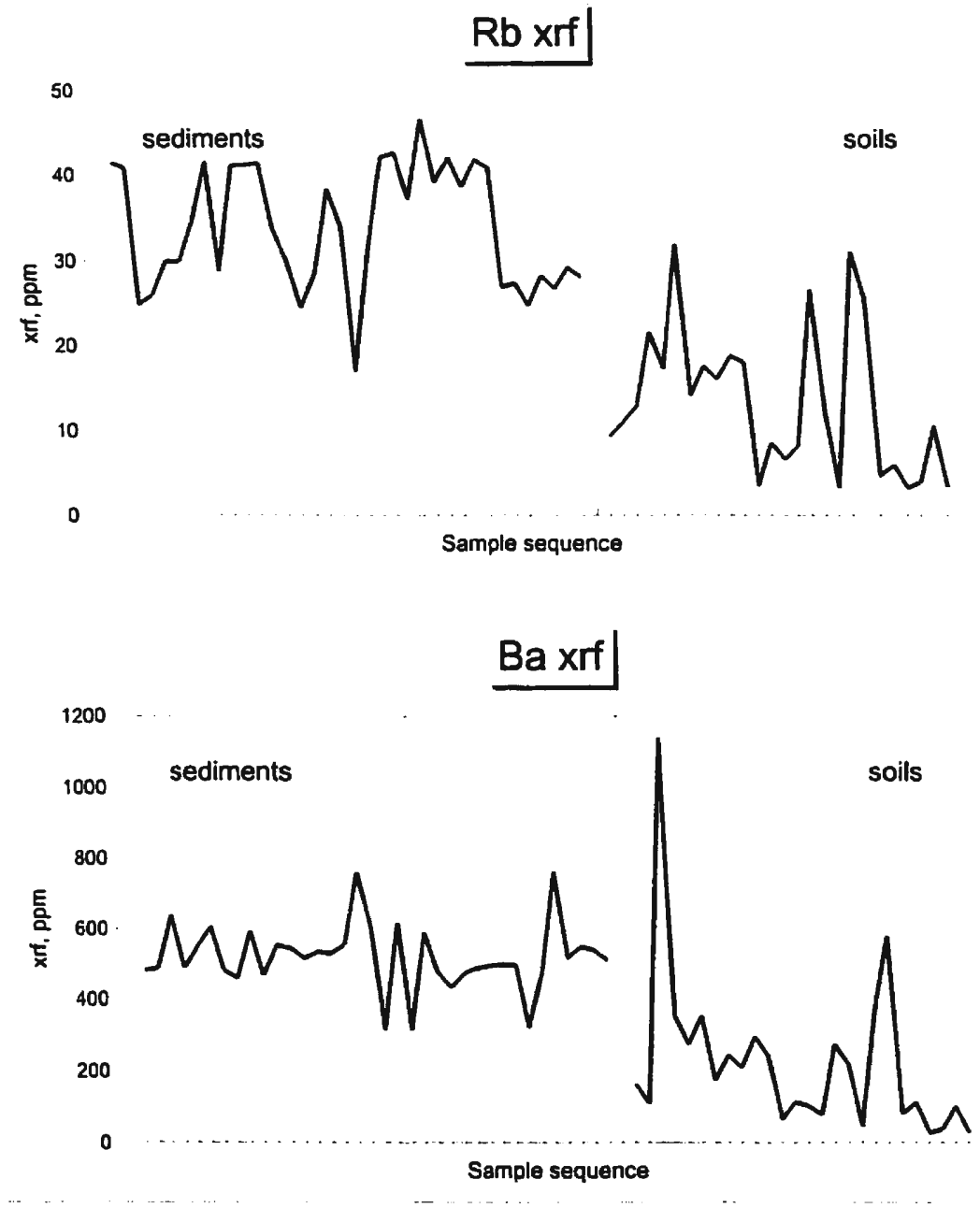

Fig. 5.11. Linegraphs showing relative Rb (above) and Ba (below) concentrations in sediments and soil samples, Cebu, Philippines.

The nickel behaviour may be associated with other analytical problems such as memory effects which caused high Ni backgrounds in the analyses (Sec. 4.7 and Sec. 4.10). However, even with the poor performance in the sediment samples, better accuracy is indicated for As and Ni in the GRMs. This appears to be influenced by the difference in particle size between these sample matrices, with the GRMs being of a finer fraction compared with the sediment and soil samples. This behaviour by As and Ni suggests that there may be a need to grind further the < 88 μm fraction to see whether a better agreement between the methods in question results.

5.7. Map Representation of Results

Urban development and industrialization can affect the geochemical landscape of an area mainly through the introduction of metals into the surficial environment. Measurement of trace element indicators often gives an indication of the current state of affairs and estimates the cumulative effect on particular sites. Stream sediments and soils reflect these changes as they are common sinks of metals released into the terrestrial environment (Adriano, 1986) although their role as potential source is also of important consideration in environmental investigation (Förstner *et al.*, 1990). Current geochemical make-up of surficial elements is now more likely a result of interaction of human activities with natural processes than of the latter alone (Christopher *et al.*, 1993).

In this Section, the geochemical landscape of the study area in Metro Cebu, Philippines, is described in terms of the distribution of transition metals and other trace elements analyzed. It was not the aim of the study to pinpoint specific sources of metal concentrations but rather to discuss source possibilities in view of existing human activities. Natural variations due to differences in the local geology is not likely significant since the whole area from where the samples were taken, along with most of the catchment area upstream, is underlain by a single lithology, i.e., limestone.

The trace element distribution in the stream sediments (Cebu City and Mandaue City) was treated separately from the element distribution in the soil samples (Lapulapu City). From each distribution was calculated the 25th, 50th (Median), 75th, 90th and 99th percentiles. The 6 geochemical classes represented by graduated circles in the maps were, as follows:

Geochemical Class	**Class Limits**	
1	*< 25th percentile*	
2	*≥ 25th*	*< Median*
3	*≥ Median*	*< 75th percentile*
4	*≥ 75th*	*< 90th percentile*
5	*≥ 90th*	*< 99th percentile*
6	*≥ 99th percentile.*	

5.7.1. Geochemical Landscape

5.7.1.1. Cebu City and Mandaue City

The distribution of the elements Cr, Ni, Cu, Zn, Pb, Sn, Sb, and Cd (Figs. 5.12 to 5.19) in the stream sediments from the cities of Cebu and Mandaue reasonably followed a trend that increased in concentration toward the coastline. With no exceptions, there were greater values in the concentration of Cu, Zn, Pb, Sn and Sb in the drainage channels within the Ayala commercial district (A-series sediment samples, refer to Fig. 5.3). Absolute concentrations were high for Cu, Pb and Sn relative to the other samples from the streams.

For Ni and Cr, the higher concentrations occur along the southwesternmost creek in the study area. Intermediate values for these 2 metals occur in the Ayala drainage ways. General increasing trend was toward the SW.

Vanadium and As (Figs. 5.20 and 5.21) showed a somewhat different distribution pattern compared with the other metals. Higher values for V appeared in the west and northwestern portion of the area while for As, there was a grouping of high values toward the north.

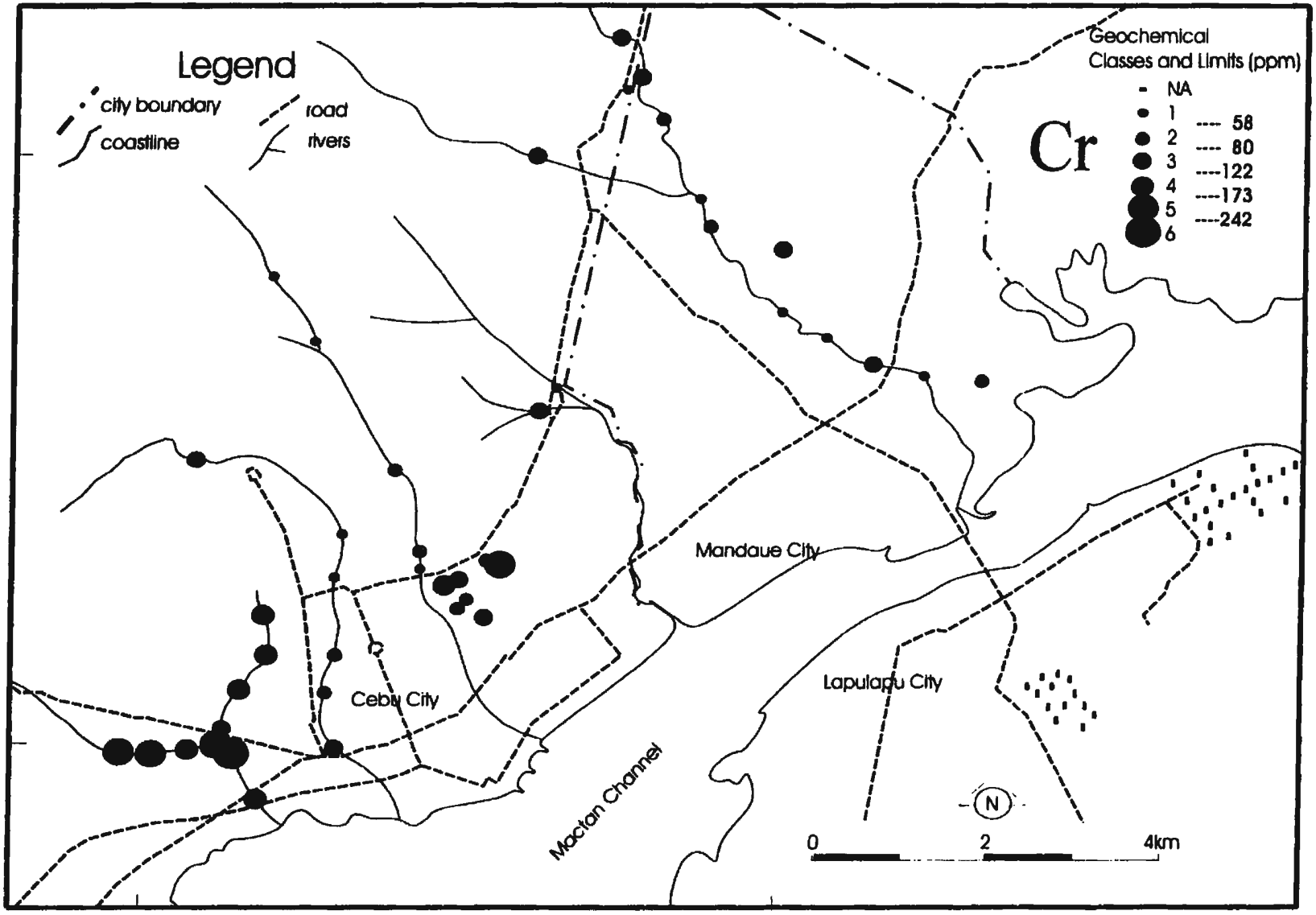

Fig. 5.12. Distribution of Cr in stream sediments, Cebu City and Mandaue City, Philippines.

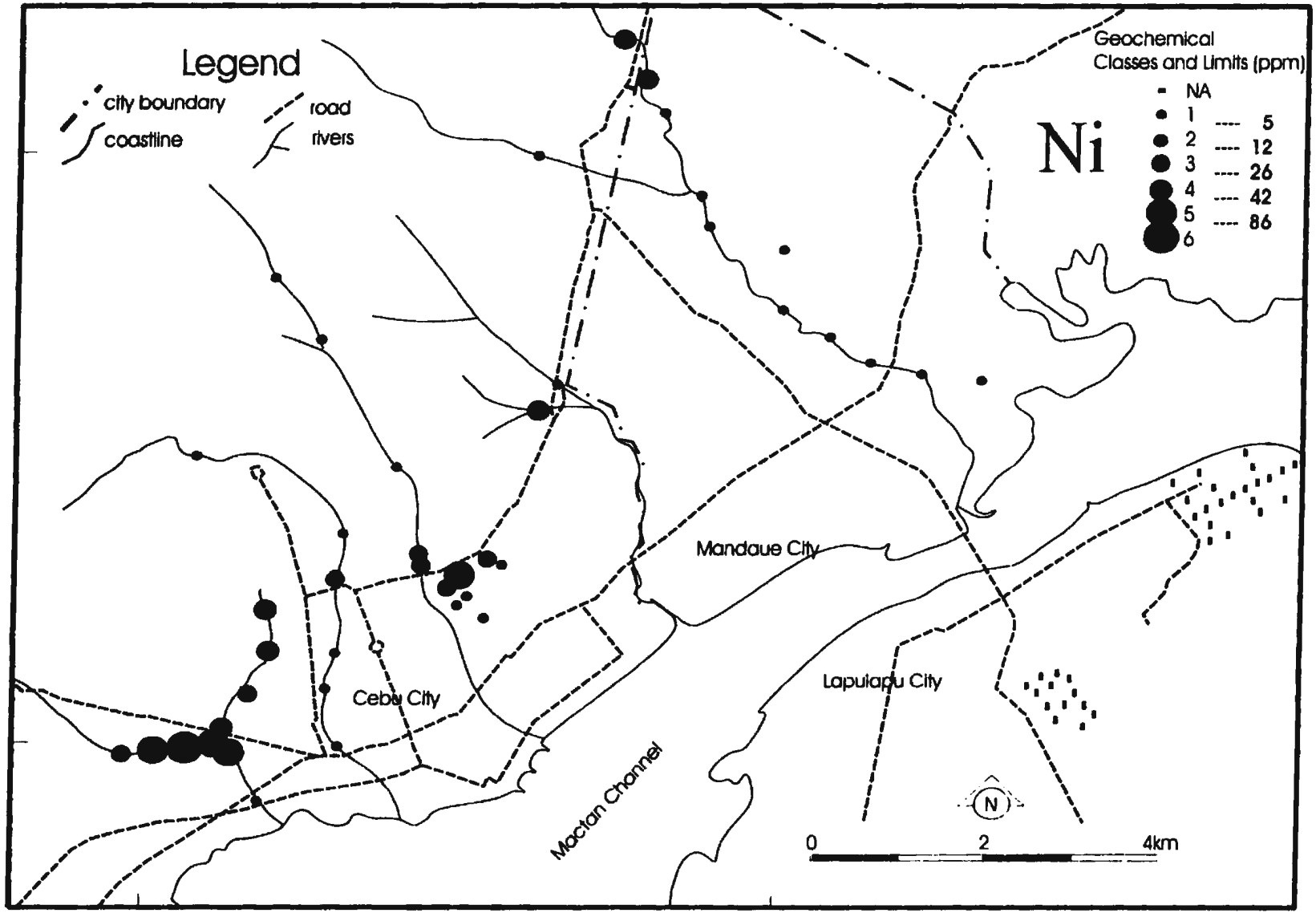

Fig. 5.13. Distribution of Ni in stream sediments, Cebu City and Mandaue City, Philippines.

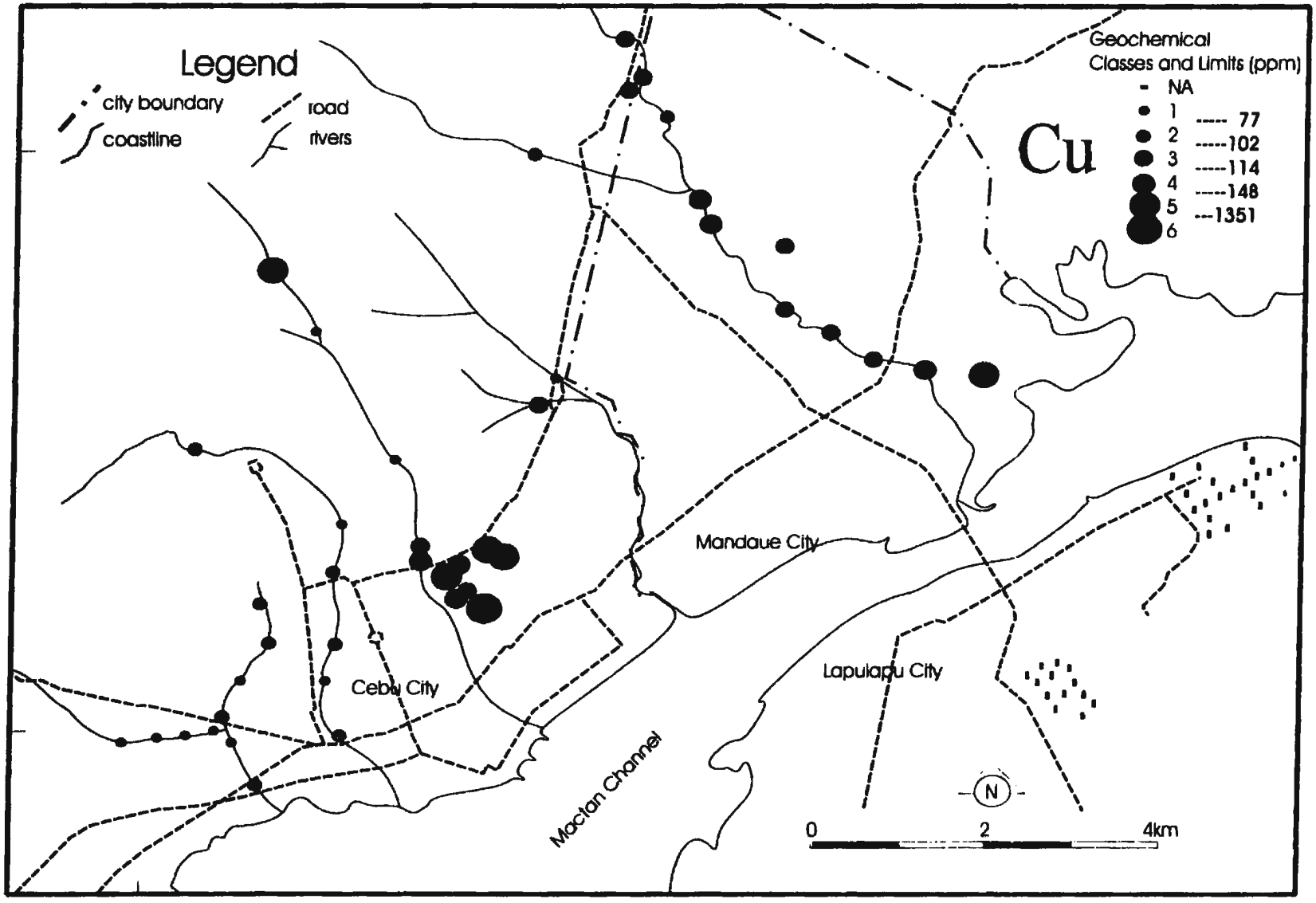

Fig. 5.14. Distribution of Cu in stream sediments, Cebu City and Mandaue City, Philippines.

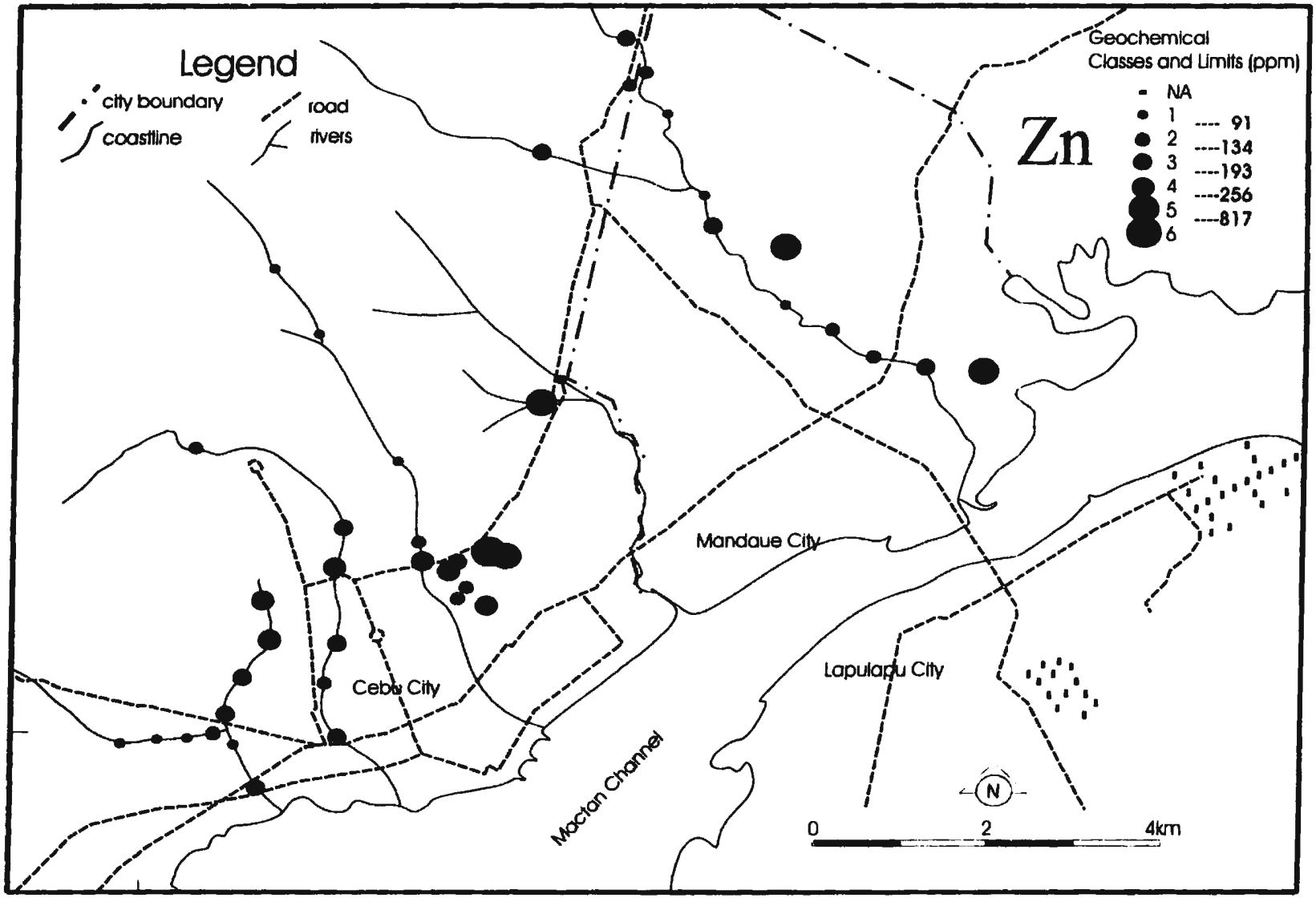

Fig. 5.15. Distribution of Zn in stream sediments, Cebu City and Mandaue City, Philippines.

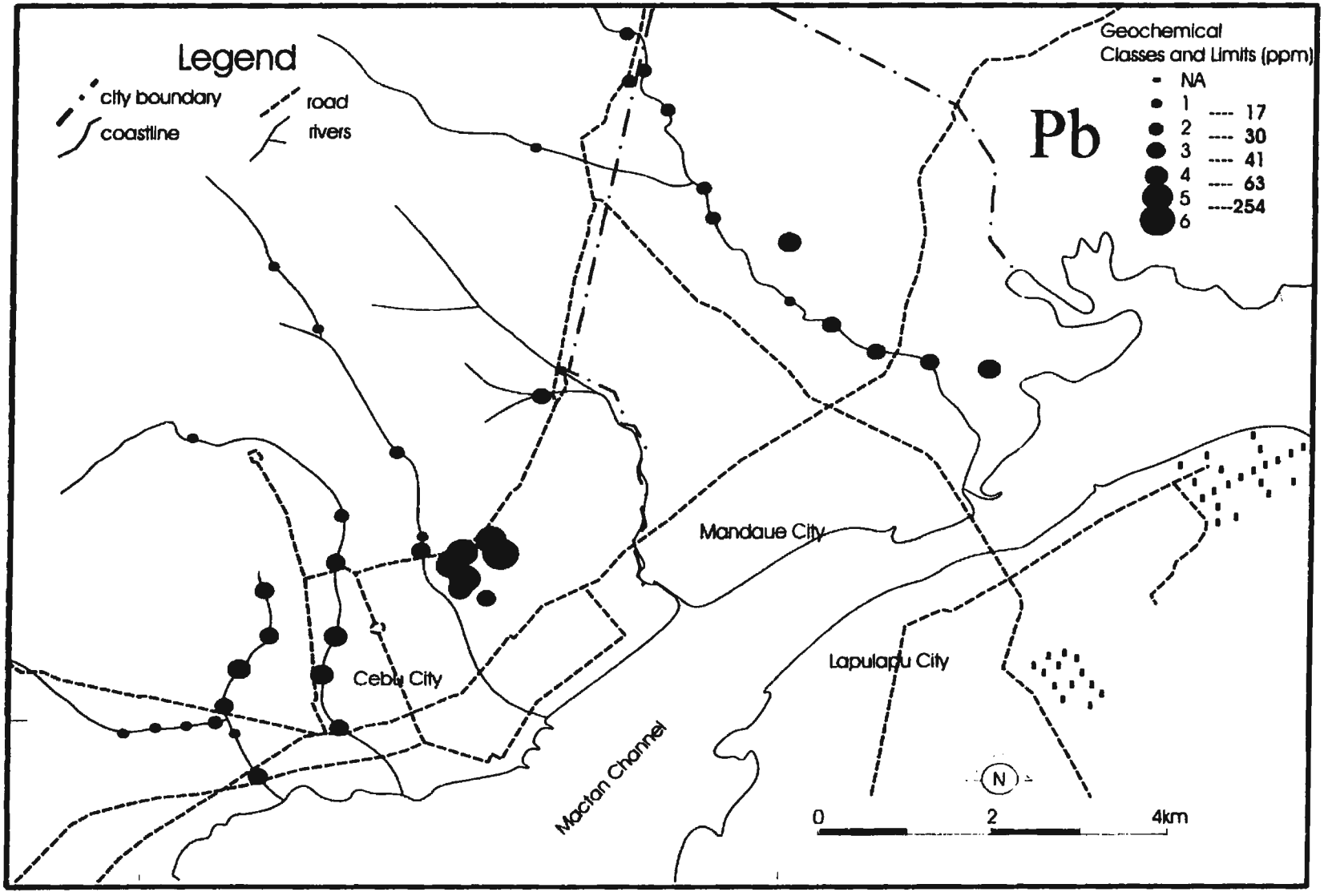

Fig. 5.16. Distribution of Pb in stream sediments, Cebu City and Mandaue City, Philippines.

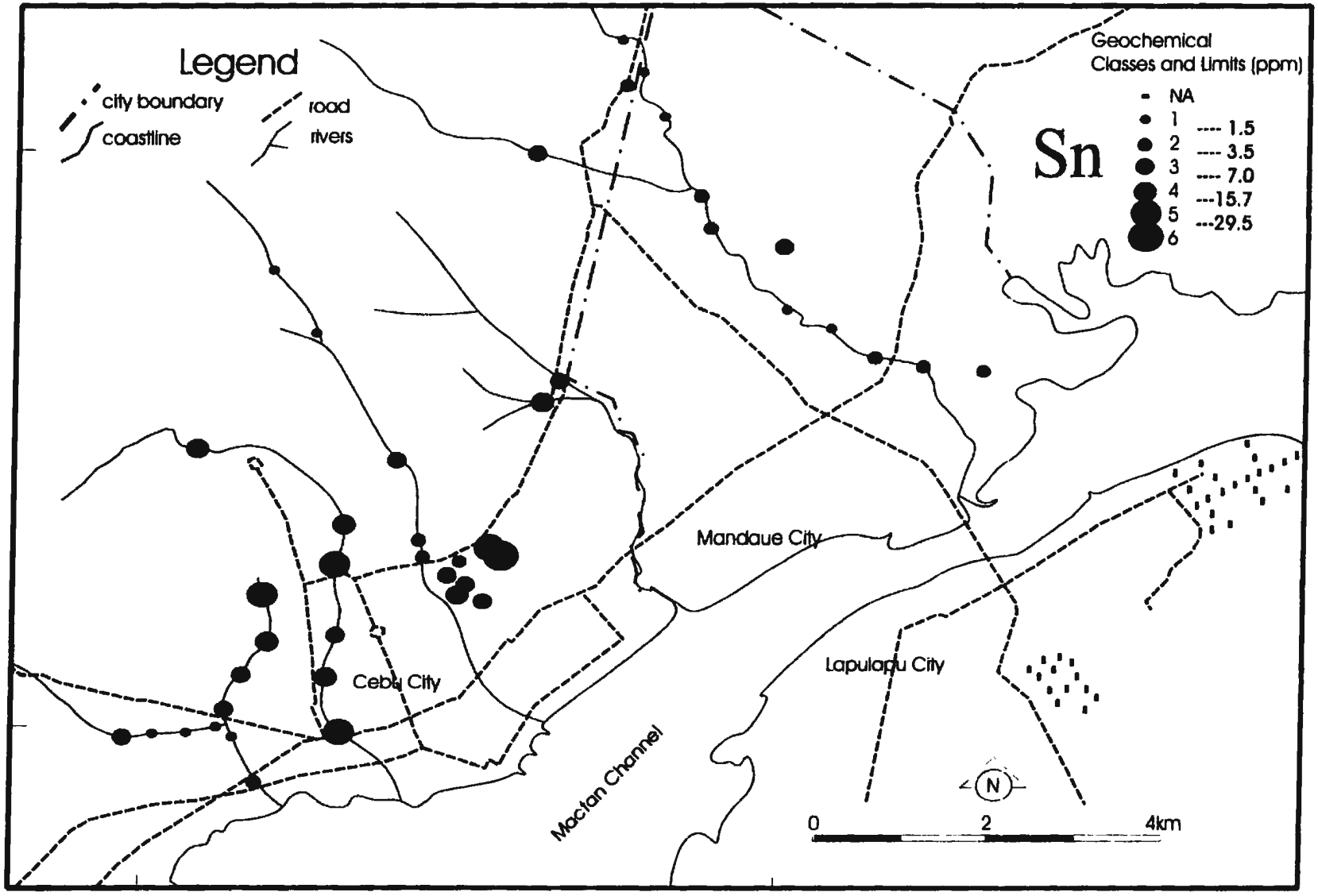

Fig. 5.17. Distribution of Sn in stream sediments, Cebu City and Mandaue City, Philippines.

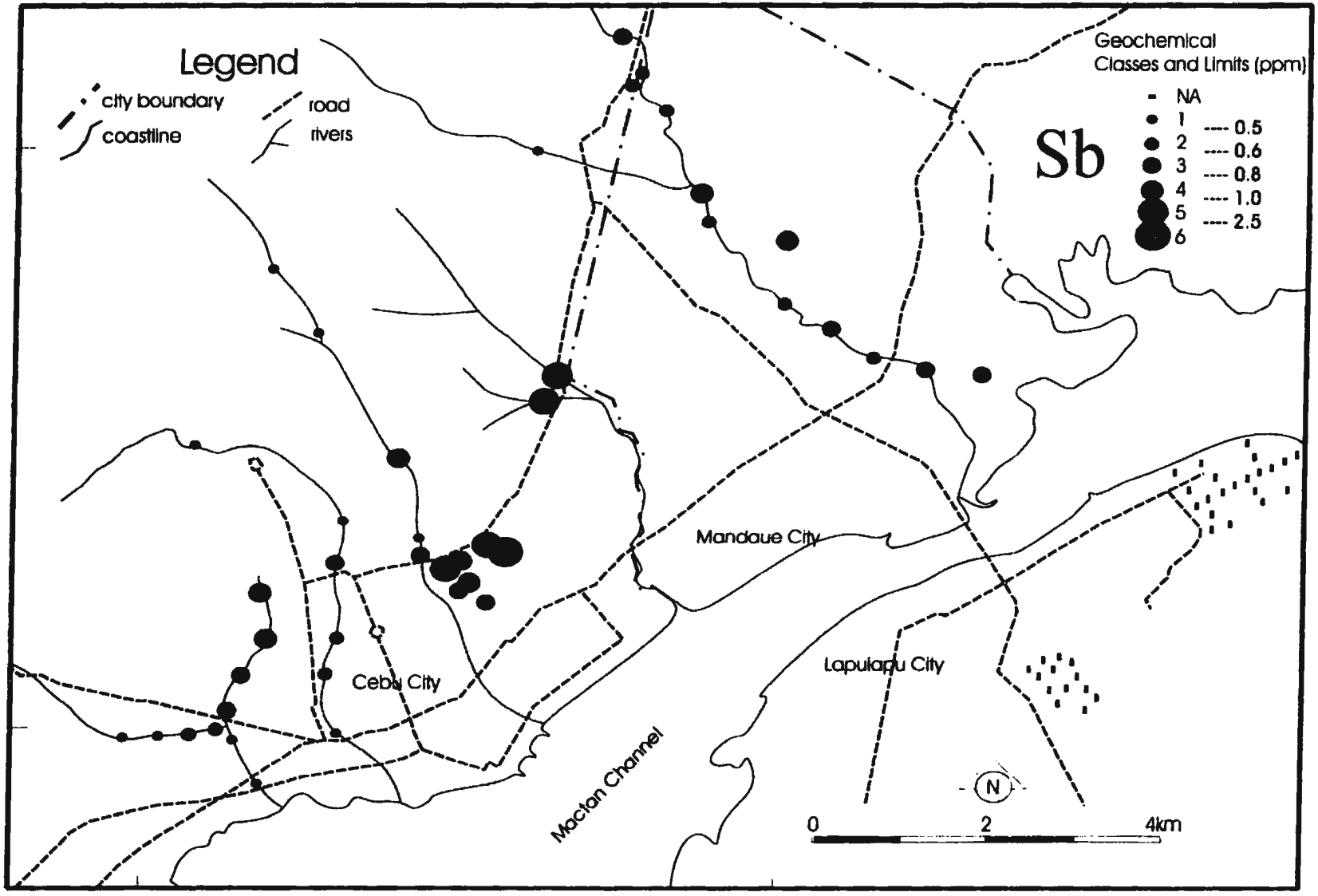

Fig. 5.18. Distribution of Sb in stream sediments, Cebu City and Mandaue City, Philippines.

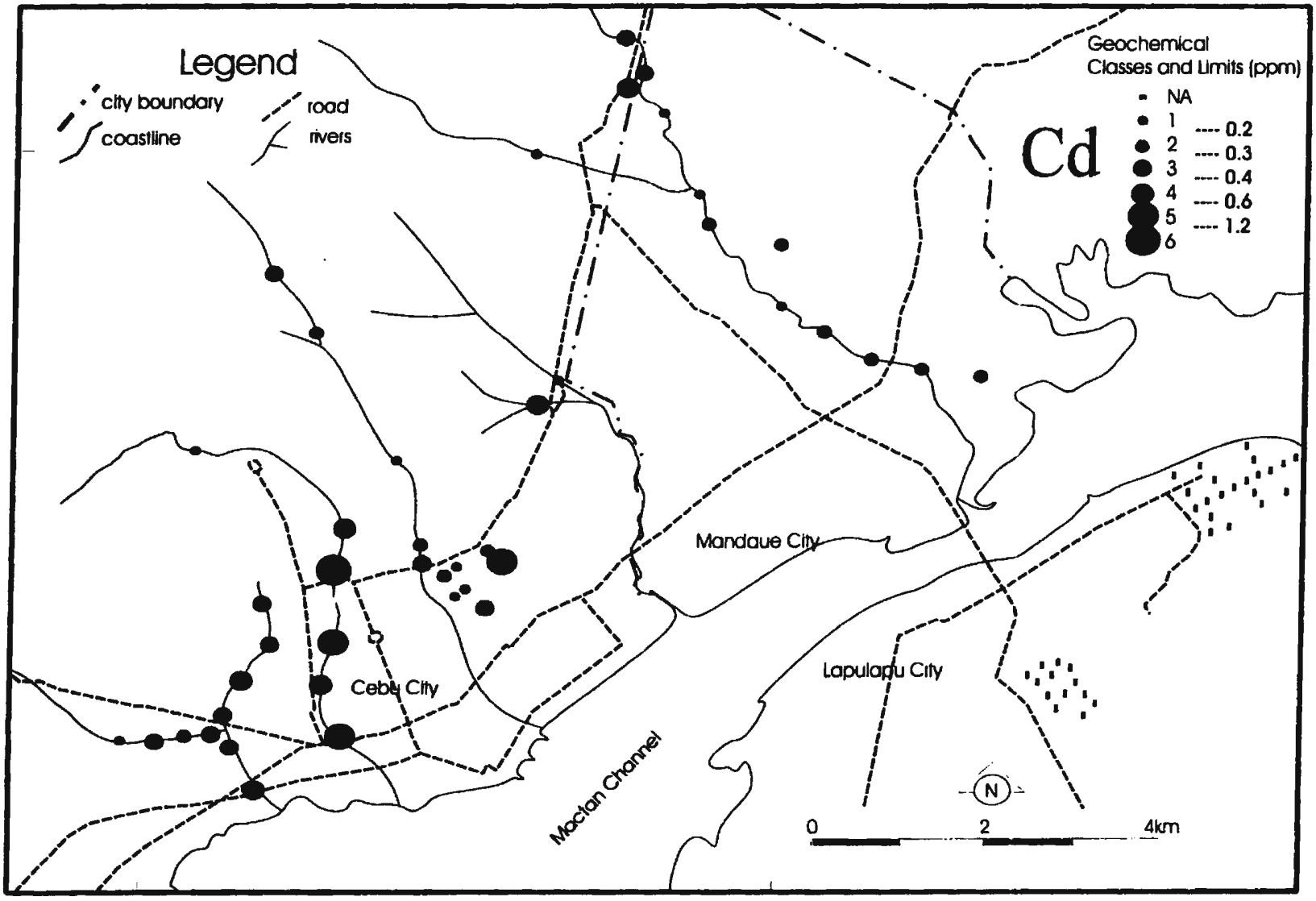

Fig. 5.19. Distribution of Cd in stream sediments, Cebu City and Mandaue City, Philippines.

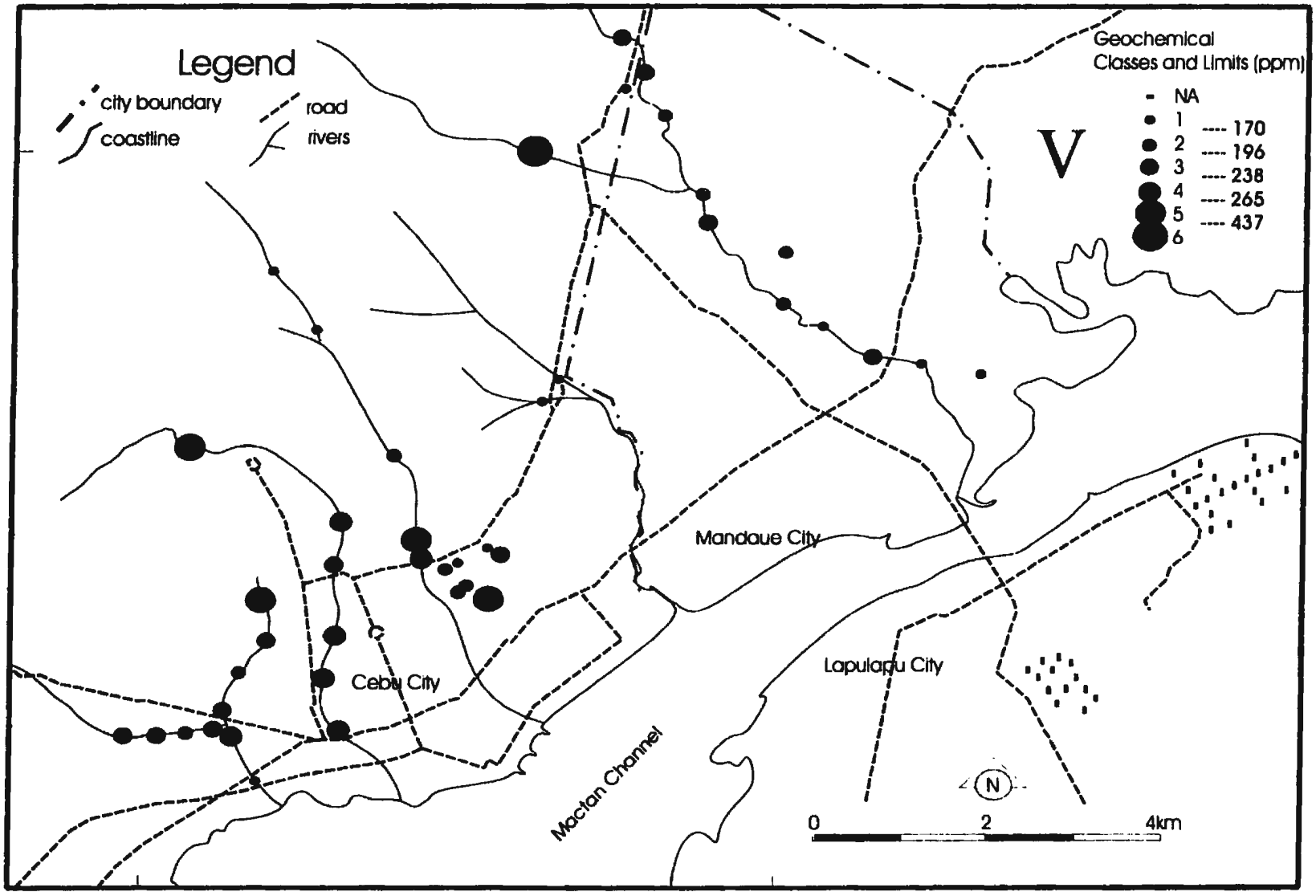

Fig. 5.20. Distribution of V in stream sediments, Cebu City and Mandaue City, Philippines.

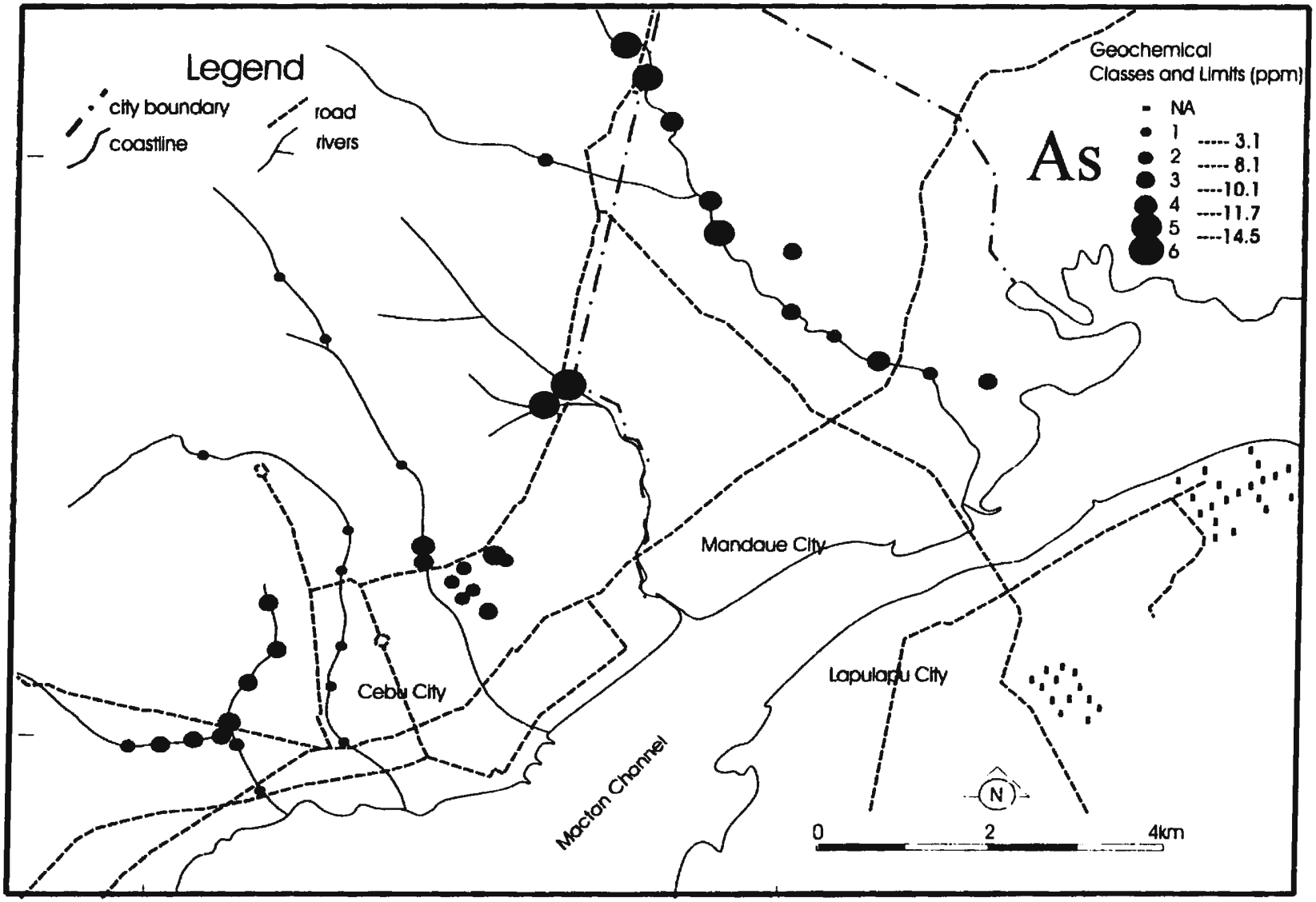

Fig. 5.21. Distribution of As in stream sediments, Cebu City and Mandaue City, Philippines.

5.7.1.2. Lapulapu City

The soil samples from MEPZ I and II in Lapulapu City generally indicated a common trend for the elements V, Cr, Ni, Cu, Zn, Cd, Sn, Sb and Pb. The first 9 elements (Figs. 5.22 to 5.30) exhibit an increasing trend toward the NE, showing higher values for the MEPZ I sub-area. Vanadium and Cr indicated some elevation along the northeast rim of MEPZ II but the higher concentrations were still in MEPZ I. The lone exception that showed elevation in MEPZ II was As (Fig. 5.31), exhibiting a significantly inverse trend in the soils compared with the other elements.

5.7.2. Implications to Possible Sources

The broad geochemical landscape described above was compared with the land-use zones (Fig. 5.4) of the metropolis. As mentioned in Sec. 5.2.2., mainly because of lack of accessibility, sampling of certain portions along the streams was not carried out. This resulted in some of the land-use zones being not well represented in the actual sampling. However, it is apparent from the general trends in the geochemical maps that high values of Cr, Ni, Cu, Zn, Pb, Sn and Sb correspond to the large area designated as a commercial zone in the southwestern portion of the map. The denser grouping of industrial zones on the eastern segment toward the coast is also indicated by higher values of the elements Cu and Zn. In the sediments along the drainage channels within the Ayala commercial district, there was an elevation of values for the elements Cu, Zn, Pb, Sn and Sb. A common

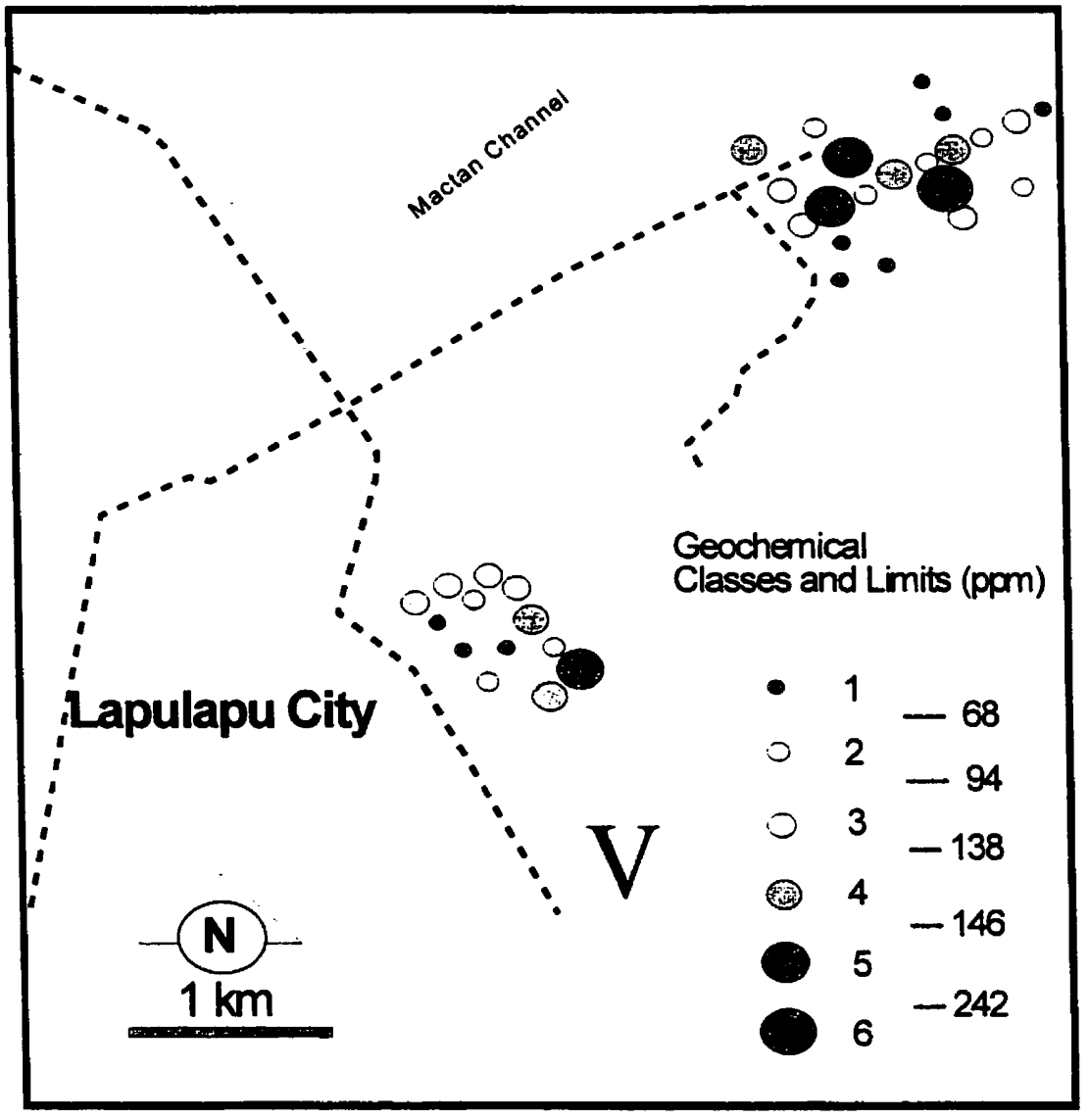

Fig. 5.22. Distribution of V in soil at MEPZ I and MEPZ II, Lapulapu City, Cebu, Philippines.

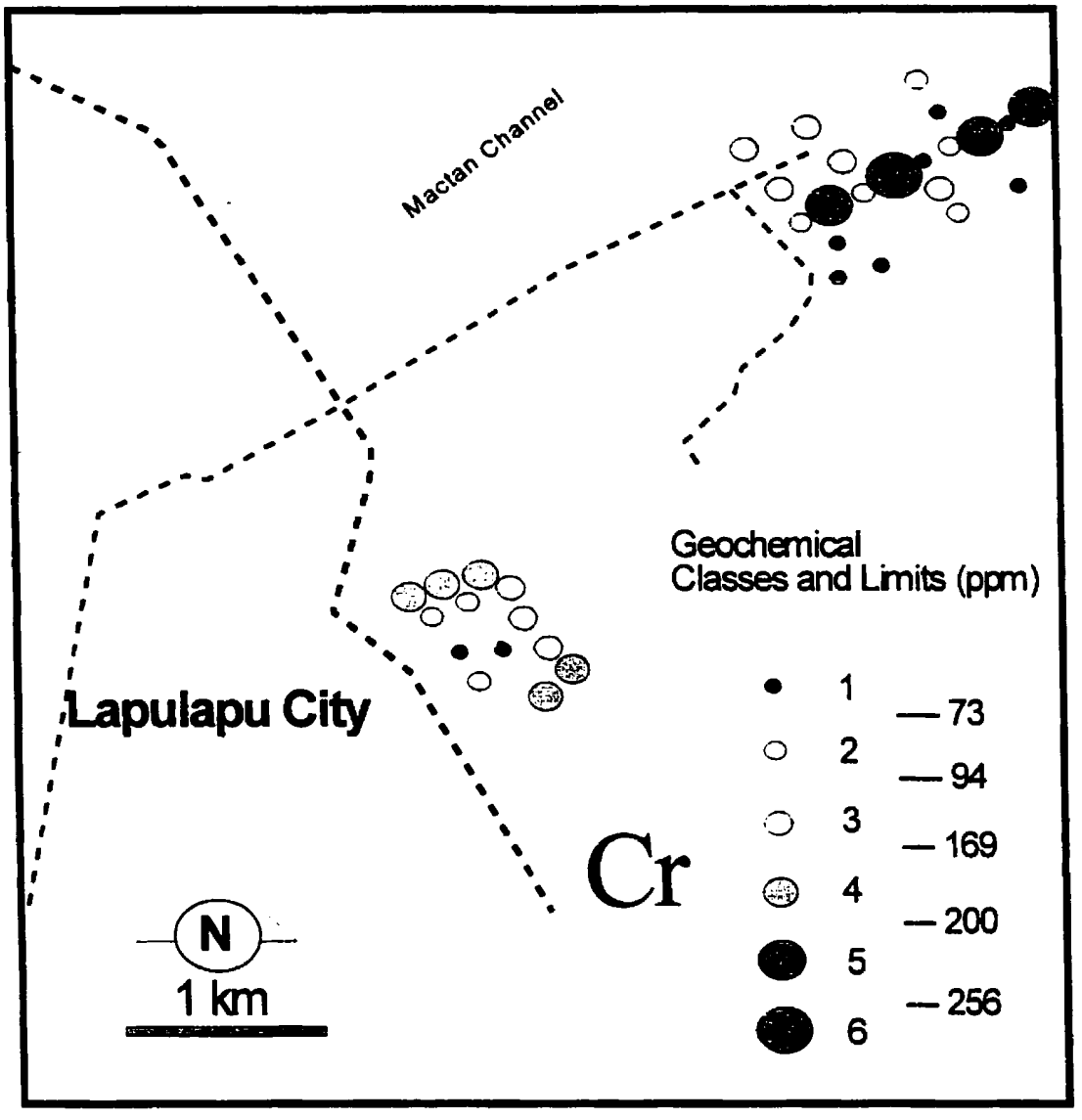

Fig. 5.23. Distribution of Cr in soil at MEPZ I and MEPZ II, Lapulapu City, Cebu, Philippines.

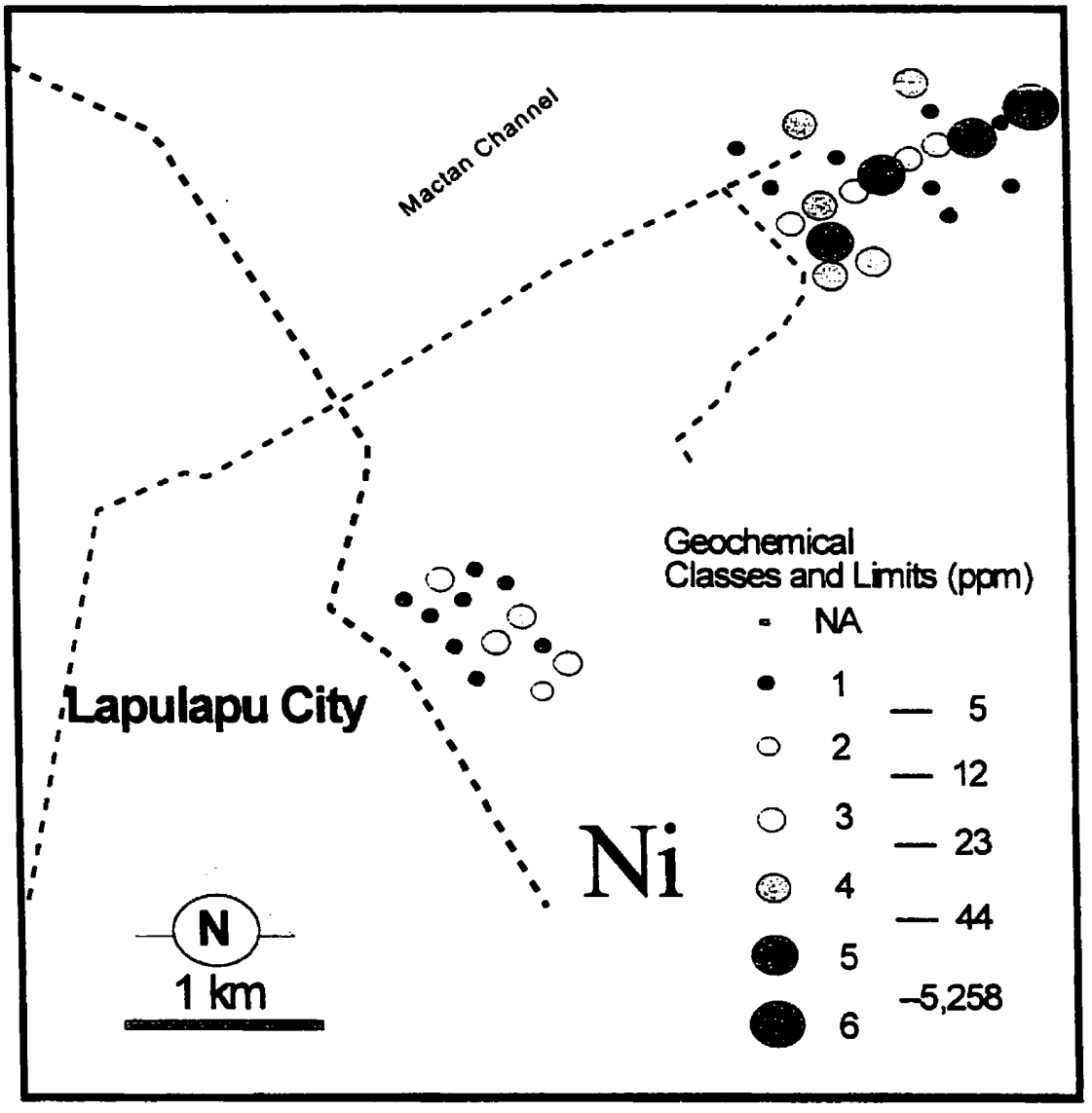

Fig. 5.24. Distribution of Ni in soil at MEPZ I and MEPZ II, Lapulapu City, Cebu, Philippines.

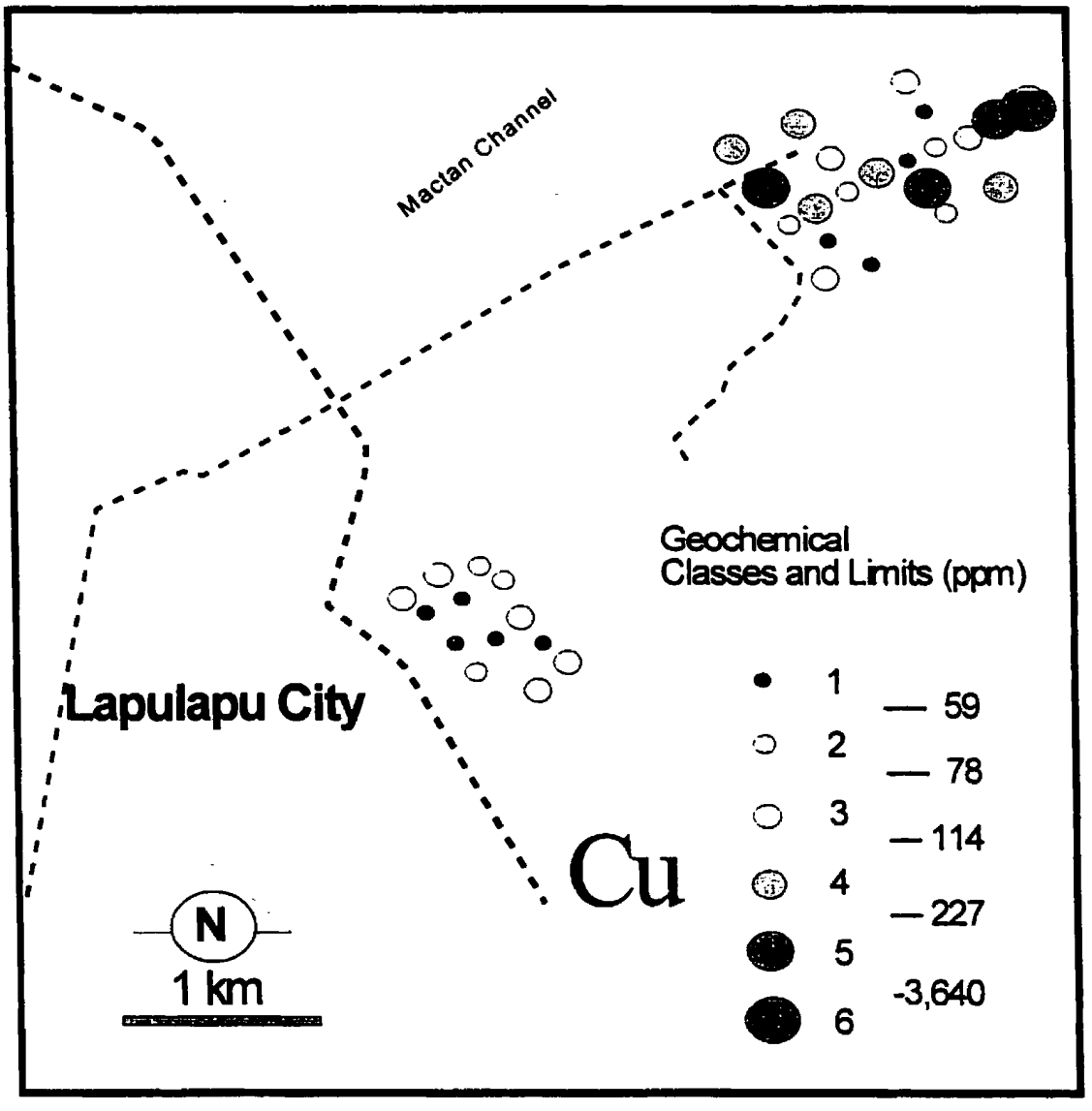

Fig. 5.25. Distribution of Cu in soil at MEPZ I and MEPZ II, Lapulapu City, Cebu, Philippines.

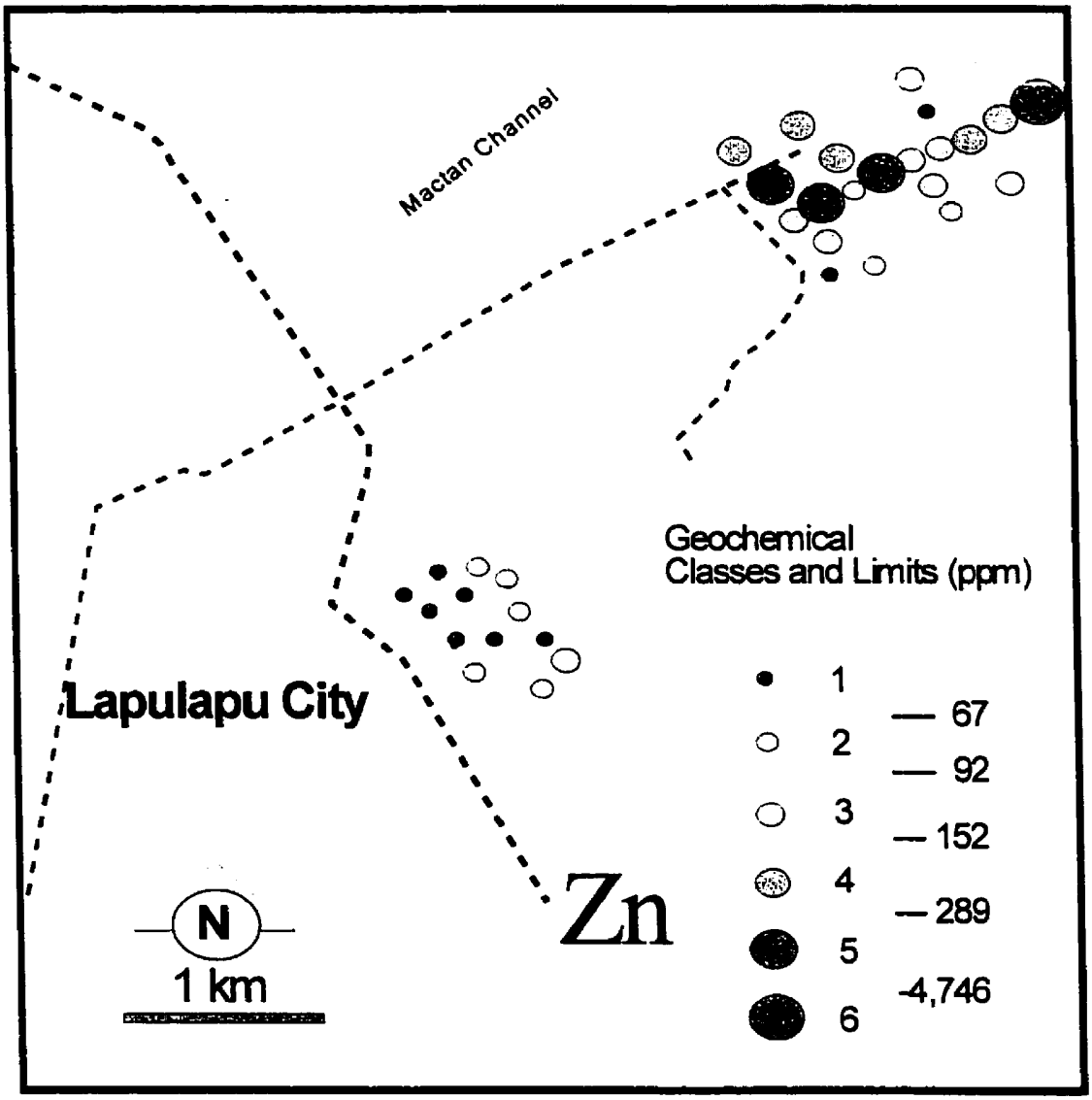

Fig. 5.26. Distribution of Zn in soil at MEPZ I and MEPZ II, Lapulapu City, Cebu, Philippines.

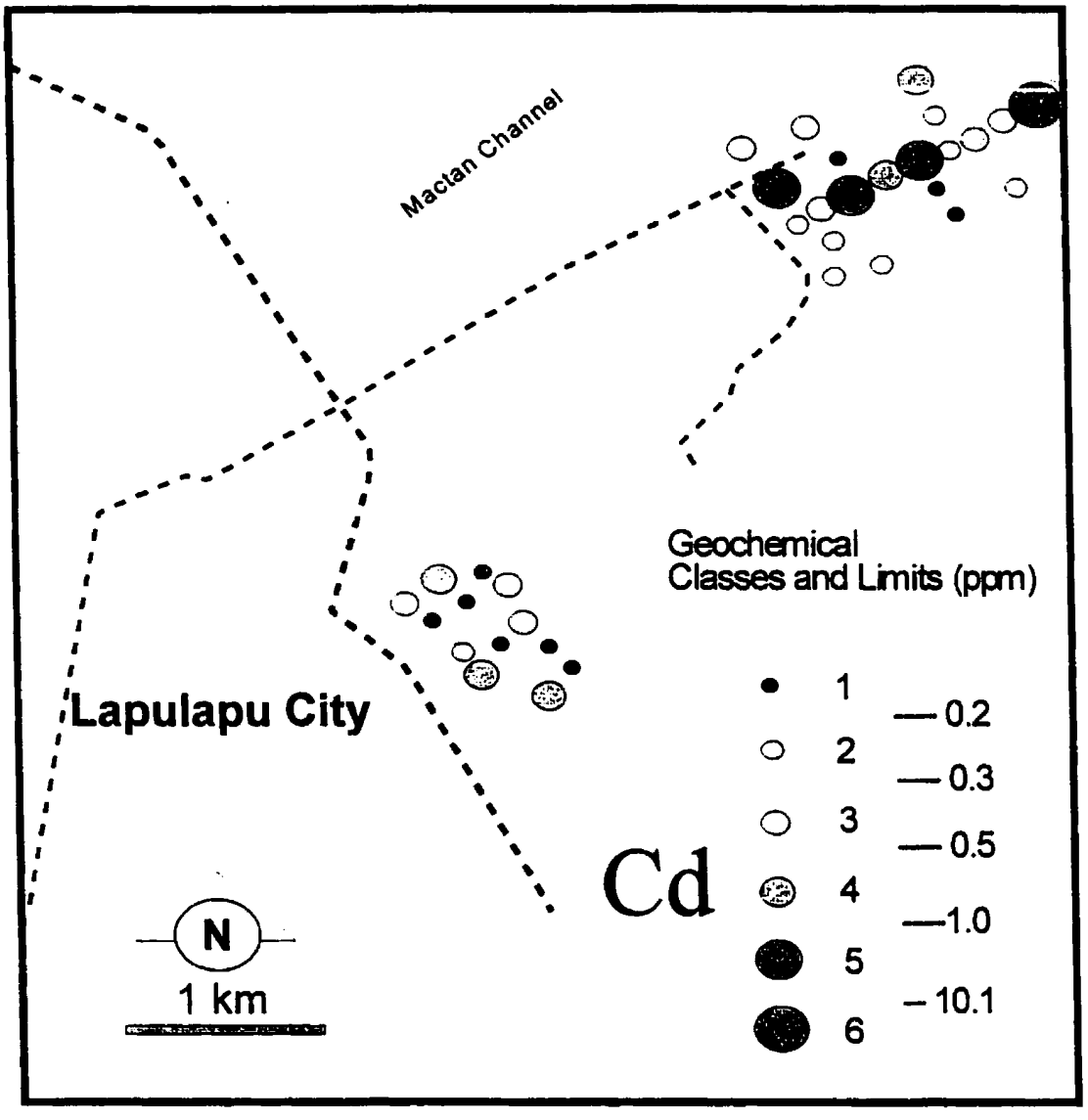

Fig. 5.27. Distribution of Cd in soil at MEPZ I and MEPZ II, Lapulapu City, Cebu, Philippines.

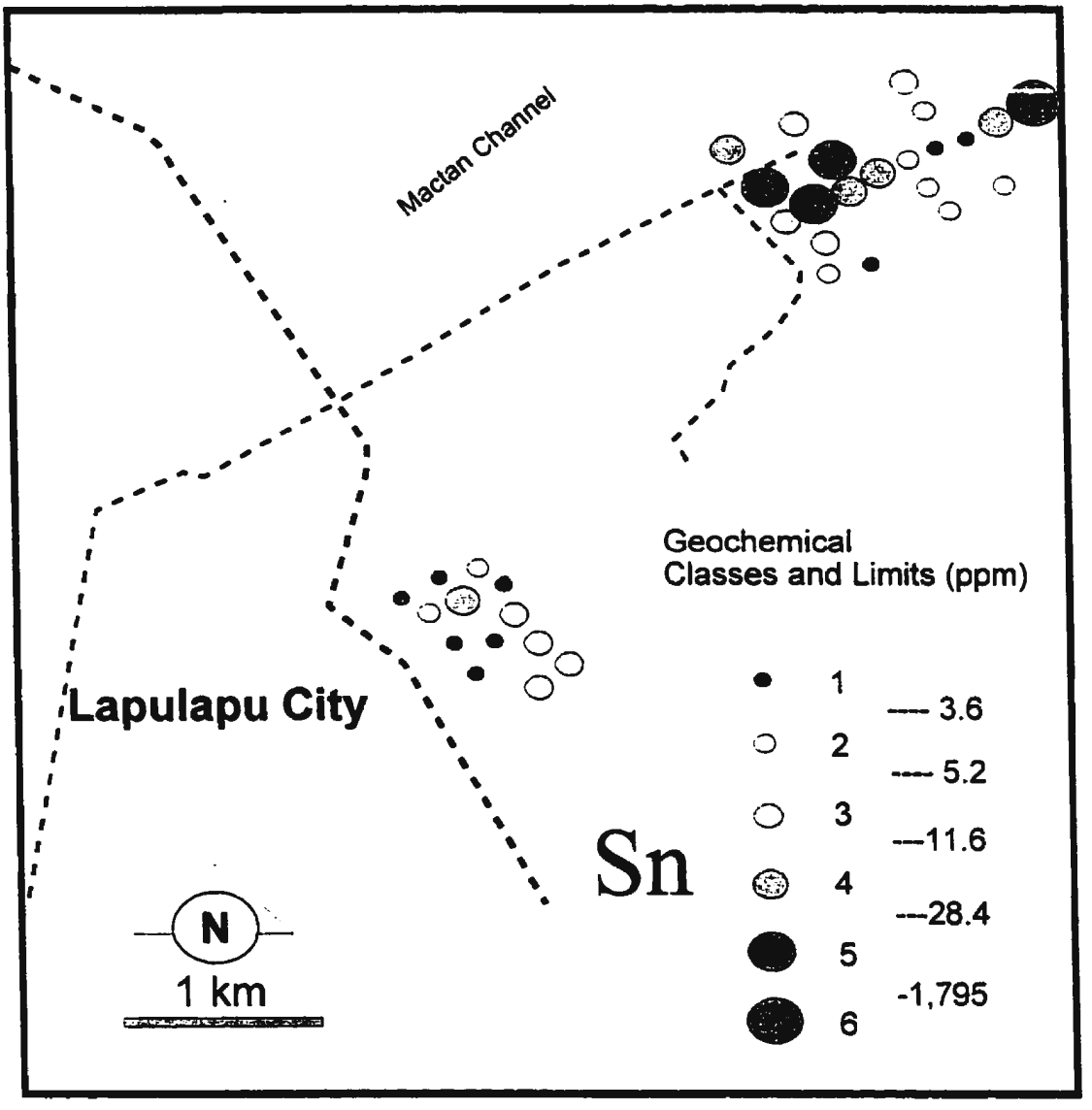

Fig. 5.28. Distribution of Sn in soil at MEPZ I and MEPZ II, Lapulapu City, Cebu, Philippines.

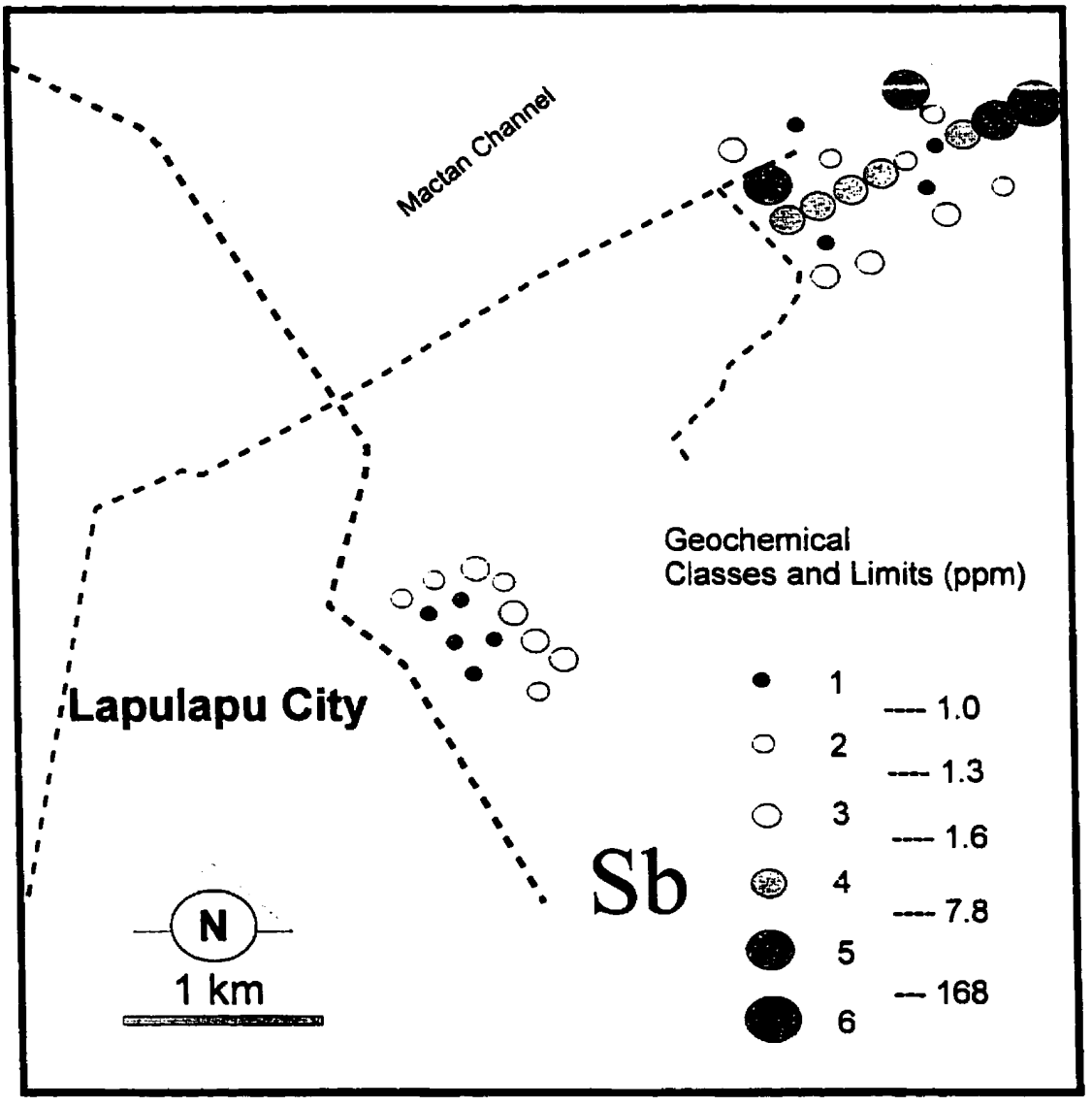

Fig. 5.29. Distribution of Sb in soil at MEPZ I and MEPZ II, Lapulapu City, Cebu, Philippines.

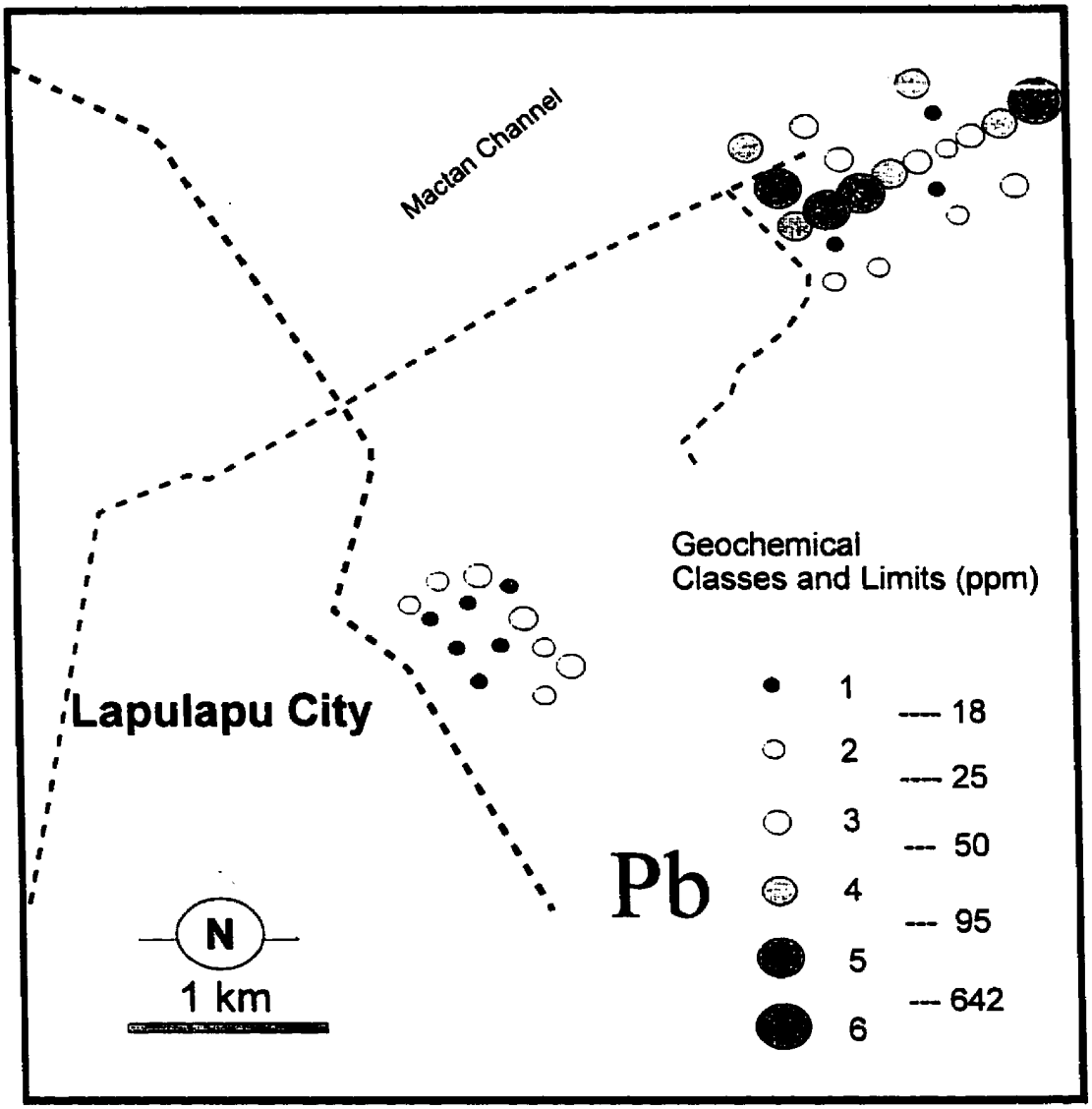

Fig. 5.30. Distribution of Pb in soil at MEPZ I and MEPZ II, Lapulapu City, Cebu, Philippines.

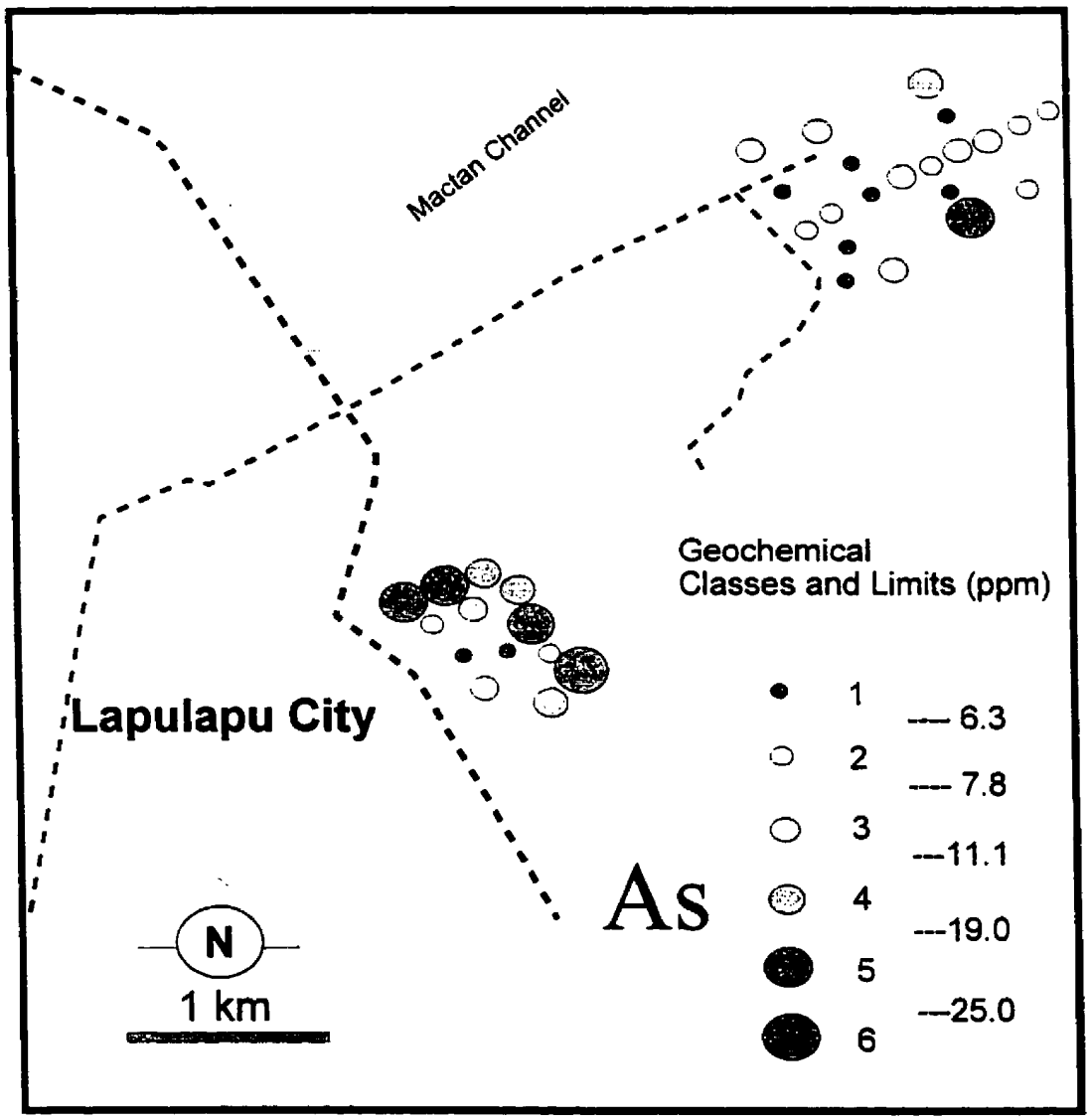

Fig. 5.31. Distribution of As in soil at MEPZ I and MEPZ II, Lapulapu City, Cebu, Philippines.

source for most of these elements is sewage effluents and sludge; however, this was not expected to play an important role as this district was a relatively new development at the time. Improper disposal of construction materials may have been responsible instead because there were several on-going construction projects during the time of sampling. Trash piles consisting of cuttings of steel bars and cables have oftentimes spilled into the channelways from adjacent construction sites.

Another probable source of Cu and Zn are Cu- and Zn-based fertilizers such as $CuSO_4 \cdot 5H_2O$ (25.5% Cu) and $ZnSO_4$ that may have been applied to landscaped lawns and grass turfs in the district. A period of heavy precipitation could easily transport loose soil material into storm drainage and sewers and into the channel ways sampled for this study. An inquiry into the type of fertilizer used for landscaping by developers in the district proved unsuccessful in determining the actual type of soil amendments employed although it was confirmed that heavy applications were the norm (J. Aleta, 1998, pers. comm). Available fertilizers in the market showed no itemization of the microcomponents except the major compounds based on nitrogen, phosphorus and potassium. It is known, however, that major commercial brands of soil amendments for landscaping purposes contain Cu and Zn among other micronutrients.

A possible source of Pb is automobile exhaust, however, traffic in the district was not as heavy as in the main thoroughfares of the metropolis. Probable source of Sn in Ayala district is organotin compounds used as fungicides since tin-plating activities are not

known in the area. The distribution of Pb and Sn was most likely a result of wires and metal items dumped near or along the drainage ways in the district. The level of Sb in the Ayala series of samples was relatively elevated compared with all the sediment samples although overall the Sb distribution was low (majority with less than 1 ppm). Any Sb in the samples could be traced to alloyed sheets and pipes that are commonly used in the area and, therefore, may have been associated with the Pb and Cu earlier mentioned. Likewise, Cd's absolute concentration is rather low; its presence may be due to sewage sludge contamination of stream sediments, or from phosphatic fertilizer and atmospheric fallout (Adriano, 1986). Incineration of plastics and Cd pigments, along with fossil-fuel burning, contribute to the airborne source cited by Adriano (1986).

Chromium and Ni showed increased concentrations in the same stream toward the SW. The association of Cr and Ni appears to indicate metal plating activity which is a common backyard-based industry in the metropolis. This area in the SW is indeed known for metal forging and finishing works, and one of the more popular, small-scale, industries in the area is the manufacture of long knives and *carets* that are popular among farmers in the agricultural fields around the area. Chromium may also be sourced from petrochemicals, foundries, steelmaking, fertilizers, leather tanning, etc. (Adriano, 1986). Much of the fertilizer use in Cebu is associated with the maintenance of mango orchards and smaller plantations located generally upstream of the settled areas.

Many trace elements such as V, B, Mo, Se, and As are commonly associated with fossil fuel combustion and atmospheric redistribution as particulates. Vanadium is an ubiquitous element in nature and easily forms organic chelates in sediments and soils. Its presence in an urban setting is mostly correlative with fossil fuel combustion whereby its release to the atmosphere is by way of particulate matter which can therefore find its way back to the ground. Alternatively, As can also be released to the environment through arsenicals used in poultry rations, pesticides and fertilizers, and in the production of coal fly ash. The highest values of As in the metropolis were near areas of intensive agriculture and therefore is correlated with fertilizer or pesticide use.

In the soil samples, all the elements cited above, except As, appear to be well correlated with each other in the MEPZ I sub-area where they gave the highest values. Activities in MEPZ I involve a variety of processes dealing with manufacture of metals, electronics, metal finishing, etc. The level of V, Cr, Ni, Cu, Zn, Cd, Sn, Sb and Pb suggests anthropogenic input and the largest impact was measured in the sample collected very close to the processing zone's incinerator. This particular site gave the maximum amount for Ni, Cu, Zn, Cd, Sn, Sb and Pb. The sampled site was actually within the compound where the incinerator building was located and in the area amidst dumped ash and stockpiled raw trash.

Arsenic was the only element that was significantly elevated in MEPZ II. With this area under extensive land development, the source of As does not appear to be related to the

introduction of chemical compounds such as fertilizers. It was not known whether herbicidal compounds were applied to the area in preparation for development. However, this portion of MEPZ II was once the site of a catchbasin that collected storm drainage from the nearby Mactan International Airport and Mactan Airbase. This was likewise the place where night soil from commercial airlines and the material from the clean-up of military planes were collected during the decades-old operation of the airport and airbase facilities before the new waste facility to the north was built 3 years ago (J. Aleta, 1998, pers. comm.). The high As levels here (greater than 19 ppm) are thus linked to an accumulation of alloys, solders, dyestuffs and electronic devices from airplane clean-up activities (Fetter, 1993).

Except for Sb and Cd, the levels of the elements in the sediment samples were higher than what was expected over a limestone terrain. The soil samples likewise indicated elevated metal levels from human activity. These elements may be sourced from a variety of factors that accompany urbanization, industrialization and intensive agriculture, the more important ones being fossil fuel combustion, sewage disposal and application of agricultural chemicals (fertilizers, fungicides, pesticides, etc.).

5.8. Summary and Conclusion

The high pressure digestion technique and the ICP-MS environmental-exploration package were applied to the analysis of the <88 μm fraction of 43 stream sediment and 34

soil samples from Cebu, Philippines. The elements analyzed were V, Cr, Mn, Co, Cu, Zn, Cd, Sn, Sb, La, Ce, Pr, Nd, Er, Tm, Lu, Pb, Bi and Th. Duplicate analysis showed an acceptable precision of 10% (RSD) or better for most of the analytes. Higher RSDs for Bi, Cd, Ag and Mo for some of the duplicate pairs were due to values below or near the detection limit.

The sample solutions were analyzed using the ICP-MS environmental-exploration package and the MUN ICP-MS trace package. Ten elements are common to both analytical protocols, and these are 7 REEs (La, Ce, Pr, Nd, Er, Tm and Lu) with Pb, Bi and Th. Comparison of the results for these 10 elements showed good agreement between the 2 analyses. Correlation coefficients calculated ranged from $r = 0.783$ for Lu to $r = 0.999$ for Ce.

The results from the ICP-MS environmental-exploration package were compared with those from the MUN XRF trace package, and good agreement was shown between the methods for the elements V, Cr, Cu, Zn and Pb, for the three sample matrices analyzed: stream sediments, soils and marine sediment reference materials. There was poor agreement at the lower end of the data scale for V and Zn, and at the upper end for Zn and Pb, and this may be due to the XRF value being out of calibration range, or to the low Zn value being due to the XRF's inherent background problems.

The results were not satisfactory for Ni and As although most of the samples gave values approaching the XRF detection limit for these elements. Nickel showed high blank concentrations, most likely due to memory effects in the ICP-MS system, necessitating the use of most of the XRF results in the geochemical landscape discussion. The review of analytical procedures from sampling handling and digestion, reagent distillation and measures against contamination, should benefit future analysis using this package. A study of the effect of concomitant elements on analyte signals should also be undertaken as this is a potential cause of signal suppression for the transition metals.

The determination of Ni and As, and perhaps other elements as well, was affected by the particle size of the analyzed sample. This was shown by the good correspondence between XRF and the ICP-MS environmental-exploration package for these elements in the geochemical reference materials (PACS-1 and MESS-2) as opposed to none in the stream sediment samples. Size analysis showed that the GRMs have a significantly larger amount of the finer size fraction compared with the stream sediment and the soil samples. Further grinding of the stream sediment and soil samples into finer fractions is likely to give better accuracy and precision compared with sieving alone.

The geochemical landscape generated appears to coincide with the known land use pattern in the area. Some of these distribution trends (e.g., for the elements Cr, Cu, Zn, Cd, Sn and Pb) clearly indicated anthropogenic input; other elements such as Sb and the REEs (which were not discussed here), showed distribution trends conforming to background

levels. In general, the high pressure digestion technique and the ICP-MS environmental-exploration package have been shown to produce reliable values for most of the elements in the analysis of stream sediment and soil samples from Cebu, Philippines.

Chapter 6

Summary and Conclusions

Trace element analysis in the earth and environmental sciences depends on accurate and precise determination of element concentration in geological samples. Analytical concerns that prevent accurate determination in the analysis of sample solutions include completeness of digestion of the samples and volatilization loss of the elements. High pressure digestion has been used to address the concern on completeness of digestion. A high pressure sample digestion method was developed at the Department of Earth Sciences, Memorial University of Newfoundland, to examine its applicability to the analysis of geological materials by solution nebulization ICP-MS.

High pressure digestion vessels, or HPDV, were fabricated from virgin teflon and machined into containers of approximately 25 ml capacity. The high pressure method was initially compared with the Department's existing method that utilizes closed vessel, low pressure digestion, using screw-top teflon (STT) jars. The comparison was made by analyzing international geochemical reference materials (GRMs) by the MUN ICP-MS trace package after digestion using the HPDV and the STT.

Results indicated good agreement between the HPDV and the STT. For 3 marine sediment GRMs, the results for Y, Zr, Nb, Hf and the HREEs, elements that are commonly associated with resistant minerals such as zircon, showed measured values that

were higher for the HPDV than for the STT, suggesting a more complete digestion of resistant minerals that are likely incorporated in the sediments.

No major difference between the 2 digestion methods was indicated for the other GRMs, except for the granite reference material, G-2. The HPDV generally gave lower values for this reference material, although Zr and Hf were significantly higher in the HPDV. These elements signify a more effective dissolution of accessory mineral constituents in the granite, most likely zircon. It can be concluded that the use of the HPDV proved successful in dissolving resistant mineral phases in materials similar to the sediment GRMs (PACS-1, MESS-2 and BSK-1) and even to the granite material (G-2), and that the method was more efficient for certain sample matrices than for others.

Results from the HPDV were also compared with results from the MUN XRF trace package and showed reasonable agreement for the GRMs PACS-1, MESS-2, AGV-1, DNC-1, SY-2 and SY-3. With XRF as a measure of completeness of digestion, having no dissolution and solution instability problems, there remains an indication of incompleteness of digestion of certain minerals by the HPDV as shown by the lower Zr in the GRMs than when the XRF was used. The HPDV can be improved in this case by lengthening the "oven" time during the dissolution stage to about 20 to 24 h. The total time allotted for this phase would still be shorter considerably than what is normally used for the STT method. The disadvantage, however, is in the number of vessels that can be used simultaneously. The STT can easily accommodate a batch that is 3- or 4-fold as many as

the HPDV.

An ICP-MS data acquisition and reduction procedure, referred to as the environmental-exploration (env-exp) package, was developed utilizing solution nebulization ICP-MS at MUN. Initial suite of analyte masses were ^{51}V, ^{52}Cr, ^{55}Mn, ^{59}Co, ^{60}Ni, ^{65}Cu, ^{66}Zn, ^{75}As, ^{77}Se, ^{79}Br, ^{98}Mo, ^{107}Ag, ^{111}Cd, ^{118}Sn, ^{121}Sb, ^{125}Te, ^{127}I, ^{139}La, ^{140}Ce, ^{141}Pr, ^{145}Nd, ^{167}Er, ^{169}Tm, ^{175}Lu, ^{183}W, ^{201}Hg, ^{208}Pb, ^{209}Bi and ^{232}Th. The most important interferences were from $^{43}Ca^{16}O$ on ^{59}Co, $^{44}Ca^{16}O$ on ^{60}Ni, $^{49}Ti^{16}O$ on ^{65}Cu and $^{50}Ti^{16}O$ on ^{66}Zn. Internal standards were ^{45}Sc, ^{115}In and ^{187}Re. ^{238}U and $^{254}(UO)$ were used to monitor polyatomic oxide formation. Sensitivities of the analyte elements were calculated from the standard solutions. However, for 3 analytes (Sn, W and Hg), surrogate calibration was performed, as there was potential for solution instability and memory effects for these elements. Solution instability may result especially for Sn in the absence of significant HF in the solution; while memory effects may result if, for example, the use of Hg in the standard solution for this package, causes Hg element to deposit in the ICP-MS system, and affect subsequent analyses. The sensitivity of Sn was calculated using that of Sb, the sensitivity of W was calculated using that of Lu, and the sensitivity of Hg was calculated using that of Pb. Only the Sn-Sb calibration was demonstrated to be successful as shown by the recovery of literature values for several GRMs. Results for Lu-W were not as definite although reasonable on a per run basis, noting that W is a common contaminant. Results for Hg-Pb were not satisfactory, and this was due, not to the calibration itself but, most probably to volatilization loss of Hg during sample digestion when the solutions were

evaporated to dryness. An alternative sample digest where the solutions are not taken to dryness should be studied in the determination of Hg from geological samples requiring acid digestion.

The ICP-MS env-exp package was used to analyze several GRMs. From the original 29 masses selected, 6 elements (Se, Br, Te, I, W and Hg) did not give good results, likely due to loss through volatilization during sample dissolution, or possibly to reagent contamination (for W). There was excellent agreement of the ICP-MS env-exp results with literature values for V, Co, Cr, Ni, Sn and Sb, except for those values close to detection limits. Reasonable agreement was shown for Cu, Zn, Mo, Cd and Pb. Results for As and Ag were rather inconclusive as values were near detection limits, except for one GRM (MESS-2) which showed excellent agreement between results of the new package and the literature value.

Compared with the MUN ICP-MS trace package results, the ICP-MS env-exp package gave good correspondence for Mo, La, Ce, Pr, Nd, Er, Tm, Lu, Pb, Bi and Th in the analysis of the MUN in-house reference material. Compared with the MUN XRF trace results, the new package showed good correspondence except for Ni, Ce and As. Nickel showed low bias in the XRF, likely resulting from an inherent Ni problem with the XRF. Generally, there was excellent agreement of results for the env-exp package with literature values as shown for several well-characterized GRMs.

The HPDV and the ICP-MS env-exp package were applied to the analysis of the < 88 μm fraction of 43 stream sediment and 34 soil samples from a metropolitan setting in the Philippines. Results from duplicate analysis showed good precision for most elements (V, Cr, Mn, Co, Cu, Sn, Sb, La, Ce, Pr, Nd, Er, Tm, Lu and Th), except for those with values near detection limits (Bi, Cd, Ag and Mo) and those likely affected by contamination during analysis or sample preparation (Pb and, less likely, Zn).

Results from all samples for 10 elements common to the ICP-MS trace package and the env-exp package (La, Ce, Pr, Nd, Er, Tm, Lu, Pb, Bi and Th) were compared, and good correlation was shown between the methods (correlation coefficient: from r = 0.783 (Lu) to r = 0.999 (Ce)). This demonstrated that the env-exp package was similarly capable of producing good and/or excellent accuracy and precision as the MUN ICP-MS trace package.

Results from all samples for 7 elements common to the MUN XRF trace package and the env-exp package (V, Cr, Ni, Cu, Zn, As and Pb) were compared, and good agreement was shown for V, Cr, Cu, Zn, and Pb for the 3 sample types represented: stream sediments, soils and GRMs. Good agreement was not shown for Ni and As. Although data points for Ni and As approached XRF detection limits, As was likely affected by volatilization loss during the ICP-MS sample digestion. It was interesting to note, however, that while the data for the stream sediments showed no correspondence between the techniques, the GRMs displayed good agreement and the soils gave reasonable agreement. A difference in

particle size between the sample types may have influenced the different responses and deserves further study.

Difference in particle size was determined by size analysis of 2 reference materials (HISS-1 and MESS-2), a stream sediment sample and a soil sample using 88 μm, 62.5 μm and 53 μm screens. It showed that the geochemical reference materials had significantly greater amounts of the finer (< 53μm) fraction. This was supported by an earlier experiment on 6 sediment samples using XRF where it indicated higher values of Ni, Cu, Zn, Ga, Sr, Y, Zr, Nb and Pb in the finer size fraction for 9 out of 11 elements. The influence of particle size suggests that there may be a need to further grind the < 88 μm size fraction to see whether a better agreement results. In general, the study of the mineralogy related to the size of the grains deserves more study not only for its sedimentological implications, but also with respect to sample dissolution procedures.

Mapping of the element data was done using 6 empirically derived geochemical classes to examine spatial distribution of the elements. Distribution of the elements Cr, Ni, Cu, Zn, Pb, Sn, Sb and Cd in the stream sediments followed an increasing trend toward the coastline. Nickel and Cr were elevated in the SW portion of the area. Vanadium had high values toward the W and NW; while for As, a grouping of higher values was to the north. The high values for Cr, Ni, Cu, Zn, Pb, Sn and Sb correspond to the large area designated as a commercial zone in the SW portion. Higher values of Cu and Zn also indicated the patch of industrial zone toward the E.

For Lapulapu City, where the soil samples were collected, all elements cited (V, Cr, Ni, Cu, Zn, Cd, Sn, Sb and Pb), except As, appear to be well correlated with each other. These elements point to the MEPZ I industrial zone which is a rather dense area of medium-scaled industries dealing with the manufacture of metal parts, electronics, metal finishing. Only As characterized the new development area of MEPZ II. Arsenic here is likely a result of accumulation from a catch basin for storm drainage that collected night soil from commercial and military airplanes using the nearby Mactan International Airport and the Mactan Airbase.

Except for Sb and Cd, the levels of the elements in the stream sediments were higher than what one would expect over a limestone terrain. The soil samples likewise indicated input from human activity. These elements may be sourced from a variety of factors accompanying urbanization, industrialization and intensive agriculture. The geochemical landscape generated appears to coincide with the known land use pattern in the area.

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Appendix A.1. Results from the two digestion methods for 3 geochemical reference materials (BSK-1, MESS-2 and PACS-1) using the ICP-MS trace package.

	BSK-1				MESS-2				PACS-1			
Element	STT(2)	std. dev.	HPDV (2)	std. dev.	STT(3)	std. dev.	HPDV (3)	std. dev.	STT(2)	std. dev.	HPDV (4)	std. dev.
Li	25.1	0.3	22.3	0.6	67	1	66	3	29.8	1.3	29.0	0.3
Rb	102.5	0.1	58.2	10.7	138	2	70	10	40	2	36	3
Sr	400	2	350	23	129	2	121	1	252	14	264	2
Y	12.6	0.6	12.8	0.9	20.4	0.3	22.7	0.3	13	1	15.6	0.3
Zr	26.3	1.1	64.5	5.3	99	2	134	5	52	3	99	10
Nb	9.0	0.4	9.2	0.8	14.4	0.3	16.6	0.7	7.9	0.6	8.9	0.3
Mo	3.070	0.003	2.9	0.1	2.9	0.1	3.0	0.1	11	1	12.6	0.5
Cs	3.24	0.01	3.06	0.13	8.6	0.2	8.1	0.1	2.1	0.1	2.21	0.03
Ba	802	11	740	6	944	8	894	23	654	14	706	18
La	23.2	1.1	19.7	2.1	37	1	36	1	16.9	0.4	16.4	0.6
Ce	46	3	40.1	2.7	74	3	71.5	2.5	34.6	1.6	35	1
Pr	5.13	0.33	4.5	0.2	8.6	0.3	8.4	0.2	4.1	0.2	4.2	0.2
Nd	18.3	1.3	16.2	0.5	32	1	31.4	1.4	16	1	16.5	0.5
Sm	3.4	0.2	3.2	0.2	5.9	0.2	5.9	0.3	3.4	0.1	3.5	0.1
Eu	0.85	0.03	0.7	0.1	1.26	0.05	1.2	0.1	0.87	0.05	1.0	0.1
Gd	2.7	0.2	2.5	0.2	4.6	0.2	4.8	0.5	3.0	0.3	3.3	0.3
Tb	0.41	0.02	0.42	0.05	0.66	0.03	0.73	0.07	0.46	0.02	0.52	0.04
Dy	2.48	0.13	2.4	0.2	3.93	0.12	4.5	0.3	2.63	0.13	3.2	0.1
Ho	0.47	0.03	0.49	0.02	0.78	0.02	0.9	0.1	0.52	0.03	0.63	0.02
Er	1.40	0.06	1.44	0.07	2.29	0.05	2.65	0.12	1.52	0.06	1.8	0.1
Tm	0.21	0.02	0.22	0.01	0.33	0.01	0.38	0.01	0.21	0.01	0.27	0.02
Yb	1.22	0.03	1.30	0.06	2.14	0.08	2.5	0.3	1.30	0.01	1.73	0.05
Lu	0.19	0.01	0.21	0.02	0.33	0.02	0.39	0.02	0.19	0.01	0.26	0.02
Hf	1.04	0.01	2.3	0.2	3.1	0.1	4.1	0.2	1.64	0.08	3.0	0.4
Ta	0.83	0.05	0.8	0.1	0.97	0.03	1.07	0.04	0.51	0.03	0.58	0.04
Tl	0.462	0.002	0.46	0.01	0.88	0.03	0.9	0.1	0.59	0.02	0.66	0.03
Pb	20.0	1.0	18.9	1.3	21.8	0.3	22.2	0.8	356	15	407	31
Bi	0.160	0.001	0.17	0.02	0.31	0.02	0.34	0.01	0.65	0.01	0.71	0.06
Th	10.4	0.6	9.6	0.6	11.6	0.8	11.3	0.8	3.95	0.14	4.2	0.2
U	2.7	0.1	2.6	0.1	3.5	0.1	3.8	0.2	2.34	0.23	2.8	0.1

STT(2) = mean of 2 replicates using screw top teflon; HPDV(4) = mean of 4 replicates using high pressure digestion vessel

Appendix A.2. Results from the two digestion methods for 3 geochemical reference materials (AGV-1, NBS-688 and BCR-2) using the ICP-MS trace package.

Element	AGV-1				NBS-688				BCR-2			
	STT(2)	std. dev.	HPDV (2)	std. dev.	STT(1)	std. dev.	HPDV (2)	std. dev.	STT(2)	std. dev.	HPDV (1)	std. dev.
Li	9.7	0.2	8.8	0.1	5.5		4.9	0.1	8.6	0.1	8.0	
Rb	68.1	0.4	53	7	1.9		1.9	0.3	47.9	0.3	48.8	
Sr	655	2	608	2	167		168	1	338	1	339	
Y	17.31	0.03	17.1	0.2	18		18	1	32.4	0.3	32.6	
Zr	224.6	0.3	218	2	53		54	1	182	1	180	
Nb	15.05	0.02	15.1	0.1	4		4.5	0.2	13.1	0.1	13.3	
Mo	2.2	0.1	2.2	0.1	0.4		0.4	0.1	263	15	302	
Cs	1.31	0.01	1.21	0.02	0.1		0.06	0.01	1.14	0.01	1.18	
Ba	1239	1	1192	5	168		178	6	684	8	685	
La	38.93	0.04	35	2	5		5.3	0.1	25.2	0.2	25.1	
Ce	70	1	65	2	12		12.2	0.2	53.4	0.3	54.9	
Pr	8.57	0.02	7.8	0.2	1.8		1.73	0.03	6.81	0.05	6.92	
Nd	31.8	0.5	30.2	0.9	8.5		8.49	0.03	28.2	0.1	28.9	
Sm	5.83	0.08	5.6	0.2	2.4		2.42	0.15	6.6	0.1	6.6	
Eu	1.68	0.06	1.6	0.1	1.0		1.02	0.00	1.96	0.05	2.17	
Gd	4.7	0.2	4.8	0.2	3.0		3.02	0.20	6.84	0.15	7.1	
Tb	0.64	0.01	0.66	0.00	0.54		0.51	0.02	1.05	0.03	1.1	
Dy	3.59	0.04	3.70	0.00	3.45		3.5	0.2	6.38	0.14	6.8	
Ho	0.69	0.02	0.71	0.02	0.76		0.75	0.01	1.29	0.02	1.36	
Er	1.86	0.01	1.9	0.1	2.2		2.2	0.1	3.63	0.15	3.95	
Tm	0.27	0.00	0.27	0.01	0.33		0.33	0.01	0.53	0.00	0.57	
Yb	1.52	0.05	1.54	0.05	2.1		2.0	0.1	3.31	0.07	3.4	
Lu	0.26	0.00	0.25	0.01	0.33		0.33	0.02	0.51	0.02	0.49	
Hf	5.67	0.05	5.6	0.2	1.79		1.69	0.02	5.37	0.18	4.94	
Ta	0.92	0.01	0.95	0.00	0.28		0.29	0.00	0.84	0.02	0.82	
Tl	0.32	0.01	0.31	0.01	0.023		0.032	0.003	0.26	0.01	0.28	
Pb	35.6	0.4	38	2	3.2		5.4	3.3	10.11	0.13	10.6	
Bi	0.055	0.001	0.06	0.01	0.01		0.02	0.01	0.06	0.01	0.06	
Th	6.35	0.05	5.96	0.04	0.36		0.35	0.03	5.86	0.03	6.0	
U	1.95	0.01	1.98	0.04	0.30		0.29	0.01	1.67	0.06	1.76	

STT(1) = value of 1 sample using screw top teflon; HPDV(2) = mean of 2 replicates using high pressure digestion vessel

Appendix A.3. Results from the two digestion methods for 3 geochemical reference materials (JB-1a, DNC-1 and MRG-1) using the ICP-MS trace package.

Element	JB-1a				DNC-1				MRG-1			
	STT(2)	std. dev.	HPDV (2)	std. dev.	STT(2)	std. dev.	HPDV (1)	std. dev.	STT(2)	std. dev.	HPDV (1)	std. dev.
Li	10.7	0.3	9.5	0.1	4.43	0.00	3.92		3.4	0.1	2.6	
Rb	38.5	0.1	38.0	0.0	3.60	0.04	3.74		7.34	0.08	6.76	
Sr	442.4	0.2	437	2	143	1	147		276	1	264	
Y	20.24	0.04	20.08	0.01	15.3	0.2	15.6		11.34	0.01	11.02	
Zr	133	2	134	3	35.1	0.1	34.8		94.8	0.3	93.4	
Nb	29.6	0.2	30.4	0.6	1.62	0.02	1.59		22.0	0.1	19.6	
Mo	1.54	0.04	1.56	0.07	0.14	0.02	0.16		1.1	0.1	0.9	
Cs	1.27	0.02	1.25	0.03	0.20	0.01	0.22		0.591	0.001	0.571	
Ba	495	1	485	1	101.4	0.2	104.6		48	1	47	
La	37.7	0.1	37.7	0.1	3.76	0.04	3.80		9.1	0.2	8.8	
Ce	66.7	0.1	67.1	0.6	8.4	0.1	8.6		26.23	0.23	25.36	
Pr	6.99	0.05	7.02	0.02	1.11	0.01	1.14		3.8	0.1	3.8	
Nd	25.9	0.2	25.6	0.5	4.90	0.01	5.29		18.4	0.5	17.9	
Sm	5.0	0.0	4.9	0.1	1.44	0.08	1.48		4.5	0.1	4.5	
Eu	1.5	0.1	1.5	0.1	0.60	0.00	0.62		1.5	0.1	1.5	
Gd	4.5	0.1	4.5	0.2	2.04	0.12	2.16		4.07	0.01	4.31	
Tb	0.7	0.0	0.7	0.0	0.38	0.01	0.39		0.57	0.01	0.61	
Dy	4.19	0.02	4.20	0.22	2.73	0.01	2.91		3.06	0.00	3.01	
Ho	0.80	0.00	0.82	0.02	0.61	0.04	0.66		0.52	0.01	0.53	
Er	2.24	0.05	2.29	0.01	1.95	0.08	2.04		1.23	0.03	1.21	
Tm	0.31	0.00	0.32	0.01	0.29	0.01	0.31		0.16	0.01	0.15	
Yb	2.00	0.07	1.9	0.1	1.91	0.02	2.05		0.77	0.03	0.89	
Lu	0.29	0.00	0.31	0.03	0.31	0.00	0.31		0.11	0.00	0.12	
Hf	3.78	0.01	3.80	0.15	1.05	0.05	1.23		3.794	0.003	4.24	
Ta	1.79	0.04	1.86	0.05	0.10	0.00	0.08		0.81	0.01	0.88	
Tl	0.09	0.01	0.11	0.01	0.02	0.00	0.04		0.05	0.01	0.04	
Pb	6.37	0.05	6.43	0.04	6.13	0.10	6.69		5.0	0.6	7.7	
Bi	0.02	0.00	0.02	0.01	0.01	0.01	0.01		0.10	0.03	0.93	
Th	9.03	0.22	9.06	0.09	0.26	0.01	0.25		0.75	0.06	0.85	
U	1.62	0.02	1.67	0.08	0.06	0.01	0.06		0.47	0.22	0.28	

STT(2) = mean of 2 replicates using screw top teflon; HPDV(1) = value of 1 sample using high pressure digestion vessel

Appendix A.4. Results from the two digestion methods for 3 geochemical reference materials (G-2, SY-2 and SY-3) using the ICP-MS trace package.

Element	G-2				SY-2				SY-3			
	STT(2)	std. dev.	HPDV (1)	std. dev.	STT(2)	std. dev.	HPDV (1)	std. dev.	STT(2)	std. dev.	HPDV (1)	std. dev.
Li	31.2	0.5	28.3		91.4	0.8	89.6		89	2	83	
Rb	170	1	94		223	4	224		209	1	201	
Sr	470	4	269		276	2	271		312	4	297	
Y	8.3	0.1	5.8		119	2	120		662	15	632	
Zr	49	1	240		288	1	294		347	16	359	
Nb	12.8	0.1	12.9		33.2	0.5	33.8		220	1	212	
Mo	0.36	0.01	0.30		0.60	0.13	0.72		0.81	0.19	1.06	
Cs	1.42	0.08	1.27		2.78	0.05	2.74		2.80	0.04	2.77	
Ba	1923	24	1862		444	1	479		442	2	431	
La	91	1	48		70.8	0.6	72.2		1304	5	1342	
Ce	169	1	70		166.0	0.6	171.4		2208	11	2270	
Pr	16.9	0.1	9.4		20.4	0.1	20.6		238.6	0.4	236.2	
Nd	54	1	31		77.3	0.6	79.3		773	13	762	
Sm	7.38	0.05	4.24		16.04	0.04	16.76		125	2	125	
Eu	1.34	0.05	1.01		2.50	0.04	2.54		18.7	0.1	18.1	
Gd	3.66	0.15	2.47		16.58	0.74	16.88		122	2	114	
Tb	0.47	0.02	0.33		3.00	0.08	3.05		21.4	0.5	20.8	
Dy	2.03	0.01	1.45		20.60	0.19	21.38		141	4	142	
Ho	0.35	0.01	0.24		4.74	0.11	4.85		31	1	31	
Er	0.84	0.02	0.62		15.79	0.22	15.75		95	2	95	
Tm	0.11	0.00	0.08		2.47	0.02	2.52		12.4	0.1	12.2	
Yb	0.37	0.01	0.33		17.79	0.52	17.56		67.5	0.1	67.4	
Lu	0.07	0.01	0.06		2.96	0.02	2.88		8.6	0.1	8.1	
Hf	1.35	0.03	6.29		8.77	0.32	8.43		10.3	0.1	9.7	
Ta	0.89	0.01	0.95		1.95	0.03	1.96		24.5	0.5	18.0	
Tl	0.90	0.03	0.91		1.53	0.03	1.58		1.43	0.02	1.53	
Pb	31.4	0.1	29.6		93.68	2.27	95.27		154.5	0.8	156.0	
Bi	0.04	0.00	0.03		0.13	0.02	0.13		0.28	0.00	0.30	
Th	24.9	0.1	14.9		371	4	376		1014	21	1001	
U	1.9	0.2	1.7		288	8	308		776	5	787	

STT(2) = mean of 2 replicates using screw top teflon; HPDV(1) = value of 1 sample using high pressure digestion vessel

Appendix B

The following is the step-by-step data acquisition and reduction procedure for the ICP-MS environmental-exploration package. Acquisition using the SCIEX ELAN ICP-MS instrument gave raw count rates in cps in a Lotus123 (*.wk1) file. Acquisition using the VG Plasmaquad gave a different format but is converted off-line into *.wk1 format.

The data reduction procedure described below starts after the data (*.wk1) has been combined into a Lotus123 (*.wk4) spreadsheet.

1) **Background calculation** - The mean of 9 "calibration blank" count rates is calculated for each analyte element. The calibration blank count rates were those obtained from 0.2M HNO_3 solutions. These background values will be used to correct gross intensities in the standard solutions and sample solutions.

For the internal standards, Sc, In and Re, zero is used. For U and UO, the background count rate of the nearby mass ^{232}Th is used.

2) **Background correction** - The gross count rates in the standard and sample solutions are corrected for the background count rates.

3) **Interference factor calculation** - The 4 most important interference factors are calculated from standard B. The interfering polyatomic ions are: $^{43}Ca^{16}O$ which interferes with the determination of Co at mass 59; $^{44}Ca^{16}O$ which interferes with the determination of Ni at mass 60; $^{49}Ti^{16}O$ which interferes with the determination of Cu at mass 65; and $^{50}Ti^{16}O$ which interferes with the determination of Zn at mass 66. The interference factors are $^{59}(CaO)/^{43}Ca$, $^{60}(CaO)/^{43}Ca$, $^{65}(TiO)/^{49}Ti$, and $^{66}(TiO)/^{49}Ti$.

4) **Correction of interference factors for matrix and drift** - Interference factors calculated from standard B are normalized to standard A by multiplying the factors by the ratio:

$$\frac{\text{mean UO/U in std B}}{\text{mean UO/U in std A}}$$

5) **Interference calculation** - The magnitude of the interference in counts per second (cps) is calculated for each tube of standard and sample solution. This is obtained by multiplying the interference factor by the intensity of the interfering element in each solution tube. For example for ^{59}Co, in one tube, the count rate of Ca which was measured at mass 43, is multiplied by the interference factor, ^{59}(CaO)/^{43}Ca. For ^{60}Ni, the count rate of Ca which was measured at mass 43, is multiplied by the interference factor, ^{60}(CaO)/^{43}Ca. For ^{65}Cu, the count rate of Ti which was measured at mass 49, is multiplied by the interference factor, ^{65}(TiO)/^{49}Ti. For ^{66}Zn, the count rate of Ti which was measured at mass 49, is multiplied by the interference factor, ^{66}(TiO)/^{49}Ca.

6) **Interference corrected for matrix and drift** - The interference calculated for a solution is corrected for matrix and drift by multiplying the value obtained in the previous step (step 5) by the ratio UO/U in the same sample solution divided by the mean UO/U ratio calculated from all standard A.

7) **Interference correction application** - The matrix and drift corrected interference obtained in the previous step (step 6) is subtracted from the background corrected intensity of the analyte.

8) **Matrix correction factor calculation** - The matrix correction factor is calculated by dividing the count rate of the internal standards (Sc, In and Re) determined by external calibration by the count rate of these internal standards in the rock solution. For example, for Sc in the first tube, the background corrected count rate measured from the first STDA solution is divided by the background corrected count rate in that same solution

giving naturally a factor of 1.00. For the second tube which is a STDB solution, the background corrected count rate measured in the first STDA solution is divided by the background corrected count rate in that second tube. This is similarly done for the third tube where the background corrected count rate measured in the first STDA solution is divided by the background corrected count rate in the third tube, and so on, until the last sample solution tube in the first cycle. For the next cycle, the background corrected count rate of the second STDA solution is used to calculate the matrix factor for the standards, blanks and sample solutions in that cycle. A factor greater than 1 indicates a suppression of the sensitivity, and hence the intensity, by the matrix of the sample relative to the dilute acid standard.

This is done for ^{115}In and ^{187}Re as well. For the analytes other than these internal standards, the matrix factor is calculated by linear interpolation and extrapolation with mass and utilizing the factors of two internal standards closest in mass to the analytes. For example, to derive the matrix factor for ^{51}V in a tube, the mass difference of ^{51}V and ^{45}Sc is divided by mass difference of ^{115}In and ^{45}Sc (2 internal standards), multiplied by the difference of the matrix factors of ^{115}In and ^{45}Sc. The resulting value is added to the matrix factor of ^{45}Sc in that tube.

9) **Instrumental sensitivity determination** - The sensitivity (cps/ppb) of each element is calculated using the given concentrations (in ppb) in the standard solutions, A and B, corrected for dilution by the pump that takes in the internal standard solution through the "Y" connector ($^2/_3$ dilution). The sensitivity (cps/ppb) of an element calculated in the standard solution is used for the sample solutions following that standard solution. Count rate data used are those previously corrected for background and interference.

10) **Surrogate calibration for Sn, W and Hg** - For 3 analytes (Sn, W and Hg), neither of the two standard solutions contain these analytes. The sensitivities of Sn, W and Hg are calculated using the sensitivities of Sb, Lu and Pb, respectively, normalized by

isotopic abundances and molecular weight. An additional correction factor, determined experimentally using a standard solution (STDC) containing the 6 analytes, was used to correct the calculated sensitivities of Sn, W and Hg. This additional factor accounts for small difference in instrumental sensitivity as a function of mass, mass discrimination and differences in fractional ionization of the two elements.

11) **Calculation of concentration in solution** - The net count rate (background and interference corrected) in cps, is divided by the calculated sensitivity (either by external calibration or surrogate calibration) in cps/ppb.

12) **Matrix correction** - The solution concentrations are multiplied by the appropriate matrix correction factor calculated in step 8.

13) **Calculation of concentration in rock** - Matrix corrected concentration in solution is divided by the dilution factor (in g/kg). Dilution factor was obtained from the actual weight of rock (approximately 0.1g) divided by actual weight of solution (approximately 60g) * 1000 * 2/3 (dilution by I.S. spike) * dilution by acid (approximately 5 g sample solution added to approximately 5 g acid in the SCIEX; 0.2 g sample solution added to approximately 9.8 g acid in the VG). This factor was approximately 0.5 g/Kg in the SCIEX and approximately 0.02 g/Kg in the VG.

14) **Calculation of limit of detection**- The limit of detection of each element is calculated using the standard deviation of the 9 blanks, the sensitivity, and the dilution of the solid in the solution.

The limit of detection is 3 times the standard deviation of the 9 blanks, divided by the background-corrected mean count rate in the standard in which the analyte is contained, multiplied by the diluted concentration in the standard, divided by the mean dilution of the run.

The detection limit for the 3 elements that are not in the standard solutions (Sn, W and Hg) is calculated using the standard deviation of the 9 blanks, the sensitivity of the surrogate element, and the dilution of the solid (surrogate) in the solution. For example, for ^{118}Sn (^{121}Sb is used): 3 times the standard deviation of ^{118}Sn in the 9 blanks, divided by the background-corrected mean count rate of ^{121}Sb in STDA, multiplied by the diluted concentration of Sb in STDA, multiplied by the natural abundance of ^{118}Sn over the natural abundance of ^{121}Sb.